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# THE CHEMISTRY OF THE CARBON COMPOUNDS

BY  
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EDITED BY THE LATE PROFESSOR  
RICHARD ANSCHÜTZ

## VOLUME III THE AROMATIC COMPOUNDS

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DEDICATED  
TO THE MEMORY  
OF  
AUGUST KEKULÉ  
BY THE EDITORS

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## PUBLISHER'S NOTE

The outbreak of the European War in 1939 interrupted our preparations for completing the third English edition based on the twelfth German edition of Richter-Anschütz, "The Chemistry of the Carbon Compounds." T. W. J. Taylor, who was in charge of the revision, assisted by Dr. Wilson, was forced, because of war time duties, to conclude his work on the manuscript at approximately page 50 of the text. But we felt obliged to provide the purchasers of the first two volumes with a complete set, as well as to meet the great demand for this treatise. Therefore, rather than have the third English edition incomplete, we decided to publish a literal translation of Volume II, part 2, of the German text without revisions and additions to the literature.

The present volume constitutes the larger portion of Volume II, part 2, of the corresponding German work. The section on organic free radicals has been shifted to the end of Volume IV, where it logically belongs.

One new feature of the present English edition is that, wherever possible, the references are given to the original journals and not to *Chemisches Zentralblatt*, and that names of the authors have been added.

We wish to express our thanks to Drs. Taylor and Wilson for the revision of the first part of the book, and to Dr. A. J. Mee and M. F. Darken for translating, editing, and checking this difficult and complex text.

October, 1945

ELSEVIER PUBLISHING CO., INC.

### SYNOPTIC TABLE OF RICHTER'S CHEMISTRY OF THE CARBON COMPOUNDS

| Subject                | TWELFTH GERMAN<br>EDITION |                        | THIRD ENGLISH<br>EDITION |                        |
|------------------------|---------------------------|------------------------|--------------------------|------------------------|
|                        | Volume                    | Year of<br>publication | Volume                   | Year of<br>publication |
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| Alicyclic Compounds    | II, Part 1                | 1935                   | II                       | 1939                   |
| Natural Products       | II, Part 1                | 1935                   | II                       | 1939                   |
| Aromatic Compounds     | II, Part 2                | 1935                   | III                      | 1946                   |
| Heterocyclic Compounds | III                       | 1931                   | IV                       | 1946                   |
| Free Radicals          | II, Part 2                | 1935                   | IV                       | 1946                   |



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## LIST OF ABBREVIATIONS

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| <b>Acta Kioto</b> .....                 | <b>Acta Scholae Medicinalis Universitatis Imperialis in Kioto.</b>                 |
| <b>Acta Physicochim.</b> . . . .        | <b>Acta Physicochimica (U. R. S. S.).</b>                                          |
| <b>Am.</b> .....                        | <b>Journal of the American Chemical Society.</b>                                   |
| <b>Am. Chem. J.</b> . . . . .           | <b>American Chemical Journal.</b>                                                  |
| <b>An. asoc. quim. argentina.</b>       | <b>Anales de la asociación química argentina.</b>                                  |
| <b>An. espafi.</b> .....                | <b>Anales de la sociedad española de física y química.</b>                         |
| <b>Angew.</b> .....                     | <b>Angewandte Chemie.</b>                                                          |
| <b>Ann.</b> .....                       | <b>Annalen der Chemie (Liebigs).</b>                                               |
| <b>Ann. chim.</b> .....                 | <b>Annales de chimie.</b>                                                          |
| <b>Ann. chim. phys.</b> .....           | <b>Annales de chimie et de physique.</b>                                           |
| <b>Ann. Physik.</b> . . . . .           | <b>Annalen der Physik.</b>                                                         |
| <b>Ann. Rep. Chem. Soc.</b> . . .       | <b>Annual Reports on the Progress of Chemistry (Chemical Society, London).</b>     |
| <b>Arch. Geneva</b> .. . . .            | <b>Archives des sciences physiques et naturelles (Geneva, Switzerland).</b>        |
| <b>Ar. Pharm.</b> .. . . .              | <b>Archiv der Pharmazie.</b>                                                       |
| <b>Atti r. accad. Lincei</b> .....      | <b>Atti della reale accademia nazionale dei Lincei.</b>                            |
| <b>Belg.</b> .....                      | <b>Bulletin de la société chimique de Belgique.</b>                                |
| <b>Ber.</b> .....                       | <b>Berichte der deutschen chemischen Gesellschaft.</b>                             |
| <b>Biochem. J.</b> .....                | <b>Biochemical Journal.</b>                                                        |
| <b>Biochem. Z.</b> .....                | <b>Biochemische Zeitschrift.</b>                                                   |
| <b>Brennstoff-Chem.</b> .....           | <b>Brennstoff-Chemie.</b>                                                          |
| <b>Bull.</b> .....                      | <b>Bulletin de la société chimique de France.</b>                                  |
| <b>Bull. acad. polon. sci. lett.</b> .. | <b>Bulletin international de l'académie polonaise des sciences et des lettres.</b> |
| <b>Bull. acad. roy. Belg.</b> .....     | <b>Bulletin d l'académie royale de médecine de Belgique.</b>                       |
| <b>Bull. Chem. Soc. Japan</b> .....     | <b>Bulletin of the Chemical Society of Japan.</b>                                  |
| <b>Bull. pin.</b> .....                 | <b>Bulletin de l'institut du pin.</b>                                              |
| <b>Bull. soc. franç. min.</b> .. . . .  | <b>Bulletin de la société française de minéralogie.</b>                            |
| <b>Bull. soc. ind. Mulhouse</b> .....   | <b>Bulletin de la société industrielle de Mulhouse.</b>                            |
| <b>C.</b> .....                         | <b>Chemisches Zentralblatt.</b>                                                    |
| <b>C. r.</b> .....                      | <b>Comptes rendus hebdomadaires des séances de l'académie des sciences.</b>        |
| <b>Can. J. Res.</b> .....               | <b>Canadian Journal of Research.</b>                                               |
| <b>Chem. and Ind.</b> .....             | <b>Chemistry and Industry.</b>                                                     |
| <b>Chem. News</b> .....                 | <b>Chemical News.</b>                                                              |
| <b>Chem. Obzor</b> .....                | <b>Chemický Obzor.</b>                                                             |
| <b>Chem. Rev.</b> .....                 | <b>Chemical Reviews.</b>                                                           |
| <b>Chem. tech. Übers.</b> .....         | <b>Chemisch-technische Übersicht.</b>                                              |
| <b>Chem. Weekbl.</b> .....              | <b>Chemisch Weekblad.</b>                                                          |

|                                |                                                                                           |
|--------------------------------|-------------------------------------------------------------------------------------------|
| Chem.-Ztg.....                 | Chemiker-Zeitung.                                                                         |
| Chim. et industrie.....        | Chimie et industrie.                                                                      |
| Current Sci.....               | Current Science (Bangalore, India).                                                       |
| Czech.....                     | Collection of Czechoslovak Chemical Communications.                                       |
| Gazz.....                      | Gazzetta chimica italiana.                                                                |
| Giorn. farm.....               | Giornale di farmacia, di chimica e di scienze affini.                                     |
| Helv.....                      | Helvetica Chimica Acta.                                                                   |
| Ind. Eng. Chem.....            | Industrial and Engineering Chemistry.                                                     |
| J.....                         | Journal of the Chemical Society (London).                                                 |
| J. Chem. Phys.....             | Journal of Chemical Physics.                                                              |
| J. Chem. Soc. Japan.....       | Journal of the Chemical Society of Japan.                                                 |
| J. Chin.....                   | Journal of the Chinese Chemical Society.                                                  |
| J. Indian Chem. Soc.....       | Journal of the Indian Chemical Society.                                                   |
| J. Indian Inst. Sci. ....      | Journal of the Indian Institute of Science.                                               |
| J. Mysore.....                 | Journal of the Mysore Agricultural and Experimental Union.                                |
| J. New South Wales .. . . .    | Journal and Proceedings of the Royal Society of New South Wales.                          |
| J. pharm. chim... ..           | Journal de pharmacie et de chimie.                                                        |
| J. Pharm. Soc. Japan .....     | Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).                          |
| J. Pharm. Ther.....            | Journal of Pharmacology and Experimental Therapeutics.                                    |
| J. Phys. Chem.....             | Journal of Physical Chemistry.                                                            |
| J. pr.....                     | Journal für praktische Chemie (Neue Folge).                                               |
| J. Roy. Tech. Coll. Glasgow .  | Journal of the Royal Technical College (Glasgow).                                         |
| J. Russ. Phys.-Chem. Soc....   | Journal of the Russian Physical-Chemical Society.                                         |
| J. Soc. Chem. Ind. Japan....   | Journal of the Society of Chemical Industry (Japan).                                      |
| J. Soc. Chem. Ind. London... . | Journal of the Society of Chemical Industry (London).                                     |
| Klin. Woch.....                | Klinische Wochenschrift.                                                                  |
| Lincei.....                    | Rendiconti della reale accademia nazionale dei Lincei. See <i>Atti r. accad. Lincei</i> . |
| Med. Rec.....                  | Medical Record.                                                                           |
| Mem. Kyoto.....                | Memoirs of the College of Science, Kyoto Imperial University.                             |
| Mikrochemie.....               | Mikrochemie.                                                                              |
| Mo.....                        | Monatshefte für Chemie.                                                                   |
| Nachr. Ges. Wiss. Göttingen.   | Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.                         |
| Org. Syn.....                  | Organic Syntheses.                                                                        |
| Pharm. Z.....                  | Pharmazeutische Zeitung.                                                                  |
| Philippine J. Sci.....         | Philippine Journal of Science.                                                            |
| Physikal. Z.....               | Physikalische Zeitschrift.                                                                |
| Physiol. Rev.....              | Physiological Reviews.                                                                    |



|                                                |                                                                                              |
|------------------------------------------------|----------------------------------------------------------------------------------------------|
| Proc.....                                      | Proceedings of the Chemical Society (London).                                                |
| Proc. Irish Acad.....                          | Proceedings of the Royal Irish Academy.                                                      |
| Proc. Roy. Soc.....                            | Proceedings of the Royal Society (London).                                                   |
| Proc. Wash.....                                | Proceedings of the National Academy of Sciences of the United States of America.             |
| Rec.....                                       | Recueil des travaux chimiques des Pays-Bas.                                                  |
| Rev. gen. sci. pures et appl....               | Revue générale des sciences pures et appliquées.                                             |
| Roczn. Chem.....                               | Roczniki Chemji.                                                                             |
| Russ. J.....                                   | Journal of General Chemistry (U. S. S. R.).<br>See also <i>Zhurnal</i> .                     |
| Schimmel's Ber.....                            | Schimmel & Co., (Halb-) Jahresbericht.                                                       |
| Science Japan.....                             | Science (Japan).                                                                             |
| Sci. Pap. Inst. Phys. Chem.<br>Res. Tokyo..... | Scientific Papers of the Institute of Physical and Chemical Research (Tokyo).                |
| Sci. Rep. Tohoku.....                          | Scientific Reports, Tôhoku Imperial University.                                              |
| Seif.-Ztg.....                                 | Seifensieder-Zeitung.                                                                        |
| Sv. Kem.....                                   | Svensk Kemisk Tidskrift.                                                                     |
| Trans. Am. Electroch. Soc....                  | Transactions of the American Electrochemical Society.                                        |
| Trans. Faraday Soc.....                        | Transactions of the Faraday Society.                                                         |
| Z. anal. Chem.....                             | Zeitschrift für analytische Chemie.                                                          |
| Z. angew. Chem.....                            | Zeitschrift für angewandte Chemie.                                                           |
| Z. anorg. Chem.....                            | Zeitschrift für anorganische und allgemeine Chemie.                                          |
| Z. Chem.....                                   | Zeitschrift für Chemie.                                                                      |
| Z. Elektrochem.....                            | Zeitschrift für Elektrochemie und angewandte physikalische Chemie.                           |
| Z. Farben-Ind.....                             | Zeitschrift für Farben-Industrie.                                                            |
| Z. Krist.....                                  | Zeitschrift für Kristallographie und Mineralogie.                                            |
| Z. Physik.....                                 | Zeitschrift für Physik.                                                                      |
| Z. physikal. Chem.....                         | Zeitschrift für physikalische Chemie.                                                        |
| Z. physiol. Chem.....                          | Zeitschrift für physiologische Chemie.                                                       |
| Zhurnal.....                                   | Zhurnal Obshchei Khimii (Journal of General Chemistry U. S. S. R.). See also <i>Russ. J.</i> |

## AROMATIC COMPOUNDS

As has been pointed out in the introduction (p. 21) to Volume II, Part I, the derivatives of benzene have characteristic properties which distinguish them from the aliphatic compounds, and also from the saturated and partially unsaturated derivatives of cyclohexane. These benzene derivatives, which are grouped together as "aromatic compounds," are divided into the following main classes:

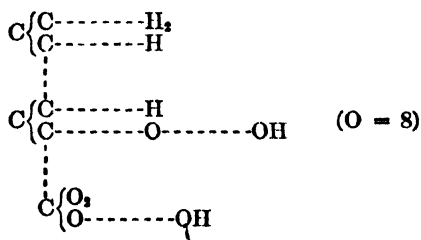
- I. Mononuclear aromatic compounds, benzene derivatives.
- II. Polynuclear aromatic compounds:
  - A. Phenyl-benzenes.
  - B. Polyphenyl-aliphatic hydrocarbons.
  - C. Compounds with condensed aromatic ring systems.

These compounds are also referred to in the introduction to Volume II, Part I. From each of these hydrocarbons and their homologues numerous derivatives of every kind are obtained, and constitute a wide and expanding field.

### I. MONONUCLEAR AROMATIC COMPOUNDS. BENZENE DERIVATIVES

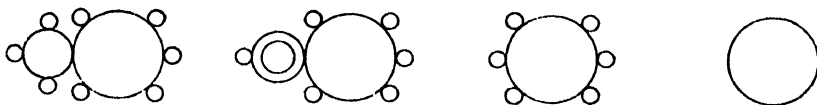
By FRANK ROCHUSSEN, ARNOLD WEISSBERGER, and  
FRITZ ARNDT, *with the cooperation of* W. BAKER,  
D. L. HAMMICK, E. HOPE, J. C. SMITH, and T. W. J. TAYLOR

The name "aromatic compounds" was originally used for substances extracted from aromatic oils and resins, and distinguished from aliphatic substances or methane derivatives in various ways and in particular by a higher percentage of carbon and a characteristic aromatic odour. A structural formula for an aromatic compound was first proposed by *Archibald Scott Couper*, who, in 1858, in a paper on salicylic acid (C.r. 46, 1107; *Ostwald's Klassiker*, No. 183, ed. by *R. Anschütz*) represented it by the formula:

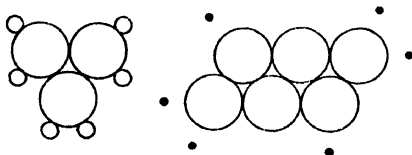


based on the type theory.

*J. Loschmidt*, in 1861, published a pamphlet, "Chemische Studien" (Vienna; *Ostwald's Klassiker*, No. 190, ed. by *R. Anschütz*) which contained new graphical formulae for 368 substances, among them 121 aromatic compounds. He was the first to regard the aromatic compounds as derivatives of the parent substance benzene: "Benzene,  $C_6H_6$ , is in the phenyl series what marsh gas,  $CH_4$ , is in the methyl series." His graphical formulae of aromatic compounds show the benzene nucleus,  $C_6$ , as a separate structural element represented by a large circle, while individual atoms are shown as small circles, e.g.,



The representation of the benzene nucleus by a larger circle was not a recognition of its ring structure. Indeed *Loschmidt* regarded the nucleus  $C_6$  as a doubled allyl nucleus, and allyl itself as trimethylene:



It cannot be inferred from these formulae that the equivalence of the six hydrogen atoms in benzene was recognised.

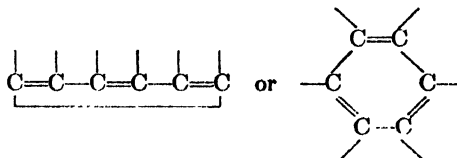
The present views on the structure of aromatic compounds have their origin in the benzene theory put forward by *Kekulé* in 1865 and expressed in his *Text-Book of Organic Chemistry*, Vol. II, p. 493 (*cf.* Ann. 137, 129) as follows:

"1. All aromatic compounds are derived from a nucleus consisting of six carbon atoms, the simplest compound containing this being benzene,  $C_6H_6$ , itself. They arise by substitution of its hydrogen atoms by other atoms or groups (the so-called side-chains); they differ from the methane derivatives, and all possess the characteristic nature of benzene; and are to be called benzene derivatives.

"2. Benzene has a symmetrical structure. Each carbon atom is jointed to a H-atom to form a carbene group,  $CH$ . As in the case of polymethylene derivatives no differences can be detected between the several C- or H-atoms, and isomerism of benzene derivatives is therefore only possible when there are two or more side-chains." (See p. 6.)

"3. The structure of the benzene nucleus (assuming that the same kind of single and double binding can occur as in the methane derivatives) is such that the six atoms or  $CH$  groups are alternately singly

and doubly bound to each other, a closed chain or ring of six carbon atoms being formed according to the scheme:



which can also be expressed as a regular hexagon. The fourth valency bond of each carbon atom in benzene is attached to a H-atom, and in its derivatives to other atoms or groups."

The first of these three propositions had been enunciated, as mentioned above, four years earlier by *Loschmidt*. Unlike *Loschmidt*, however, *Kekulé* put forward a structure for the  $C_6$  nucleus itself which fitted into the framework of his organic structure theory based on the "four affinities" of the carbon atom. This is expressed in the third of the propositions quoted. The equivalence of the six hydrogen atoms in benzene (proposition 2) which at the time was becoming more and more clearly established was expressed graphically by *Kekulé's* formula, which gave an impetus to further experimental work on this point, and a lead to the investigation of aromatic compounds in general (*Anschutz*, Ber. 45, 539). Nowadays all compounds containing the benzene nucleus are classed as aromatic substances, and the characteristic properties of aromatic compounds are also recognised in other classes of substances, *e.g.*, members of the thiophene and pyridine series (p. 5).

### Survey of the Benzene Derivatives

The benzene derivatives are derived from benzene just as the aliphatic compounds are derived from methane, by replacing (substituting) the hydrogen atoms with other atoms or groups of atoms. Benzene derivatives with side-chains containing carbon can be built up from benzene, and can be reconverted into it by elimination of the side-chains.

Benzene derivatives differ from methane derivatives in the stability of the benzene nucleus. Oxidation, while destroying the side-chains, usually fails to attack the benzene nucleus. This is also the case with reduction. Under suitable conditions reduction may lead to the addition of hydrogen to the benzene nucleus with the formation of cyclohexane derivatives, but the ring is not ruptured. This addition of hydrogen shows the relation between the derivatives of benzene and those of cyclohexane (*cf.* Vol. II, p. 82).

Most benzene derivatives which are solid at ordinary temperature crystallise with ease, and this is a great aid in experimental work.

According to the number of hydrogen atoms in the benzene nucleus which are replaced, mono-, di-, tri-, tetra-, penta-, and hexa-derivatives of benzene are obtained.

The hydrogen of benzene is readily replaced by chlorine and bromine, by the nitro-group,  $\text{NO}_2$ , and by the sulphonic acid group,  $\text{SO}_3\text{H}$ :

|                        |                                           |                                               |                                                      |
|------------------------|-------------------------------------------|-----------------------------------------------|------------------------------------------------------|
| Chlorobenzenes         | $\text{C}_6\text{H}_5\text{Cl}$           | $\text{C}_6\text{H}_4\text{Cl}_2$             | $\text{C}_6\text{H}_3\text{Cl}_3 \dots \text{CCl}_6$ |
| Nitrobenzenes          | $\text{C}_6\text{H}_5\text{NO}_2$         | $\text{C}_6\text{H}_4(\text{NO}_2)_2$         | $\text{C}_6\text{H}_3(\text{NO}_2)_3$                |
| Benzenesulphonic acids | $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ | $\text{C}_6\text{H}_4(\text{SO}_3\text{H})_2$ | $\text{C}_6\text{H}_3(\text{SO}_3\text{H})_3$        |

A very characteristic reaction of benzene derivatives is the formation of nitro-compounds by the direct action of nitric acid, and of sulphonic acids by the action of sulphuric acid; paraffin hydrocarbons are usually unaffected by these reagents, and other aliphatic compounds are generally oxidised or decomposed by nitric acid.

Reduction of the nitro-compounds gives aromatic *amines* such as aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ , phenylene diamine,  $\text{C}_6\text{H}_4(\text{NH}_2)_2$ , etc.

By the action of nitrous acid on the amino-compounds aromatic *diazo*-compounds are produced, a class of compounds which have but few analogues in the aliphatic series.

When the hydrogen atoms of benzene are replaced by hydroxyl groups, *phenols* are obtained:

|                                 |                                     |                                     |
|---------------------------------|-------------------------------------|-------------------------------------|
| $\text{C}_6\text{H}_5\text{OH}$ | $\text{C}_6\text{H}_4(\text{OH})_2$ | $\text{C}_6\text{H}_3(\text{OH})_3$ |
| Phenol                          | Dihydroxy-benzenes                  | Trihydroxy-benzenes                 |

Like the tertiary alcohols the phenols contain the group  $\text{C}\cdot\text{OH}$  linked to carbon, and consequently cannot be oxidised to aldehydes, ketones, or acids.

In the amino derivatives of benzene the basicity of an amino group directly attached to the ring is considerably weaker than it is in the aliphatic amines. Correspondingly, the hydroxyl group in the phenols is more acidic than in the alcohols.

The homologous benzene hydrocarbons, saturated and unsaturated, are derived from benzene by the introduction of monovalent alkyl, olefinic, or acetylenic residues:

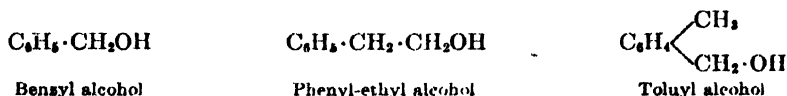
|                        |                                             |                                       |                                                      |                                                   |
|------------------------|---------------------------------------------|---------------------------------------|------------------------------------------------------|---------------------------------------------------|
| $\text{C}_6\text{H}_6$ | $\text{C}_6\text{H}_5\cdot\text{CH}_3$      | $\text{C}_6\text{H}_4(\text{CH}_3)_2$ | $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{CH}_3$    | $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ , etc. |
| Benzene                | Methyl-benzene<br>(Toluene)                 | Dimethyl-benzene<br>(Xylene)          | Ethyl-benzene                                        | Propyl-benzene                                    |
|                        | $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ |                                       | $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ , etc. |                                                   |
|                        | Vinyl-benzene (Styrene)                     |                                       | Phenyl-acetylene                                     |                                                   |

In these hydrocarbons the benzene residue retains the characteristic properties of benzene. Its hydrogen atoms are easily replaced by halogens or the  $\text{NO}_2$  or  $\text{SO}_3\text{H}$  groups. On the other hand, the side-chains behave like aliphatic hydrocarbons. Their hydrogen atoms can be replaced by halogen, but not by the groups  $\text{NO}_2$  or  $\text{SO}_3\text{H}$  by the action of concentrated sulphuric or nitric acids, respectively. According as whether the halogens (or other groups) enter the benzene residue or a side-chain, different isomers are formed:

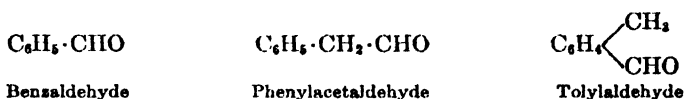
|                 |                                                   |                                          |                                                          |
|-----------------|---------------------------------------------------|------------------------------------------|----------------------------------------------------------|
| Chlorotoluene   | $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_3$   | Benzyl chloride                          | $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{Cl}$          |
| Dichlorotoluene | $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CH}_3$ | Chloro-benzyl chloride                   | $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Cl}$ |
|                 | Benzylidene chloride                              | $\text{C}_6\text{H}_5\cdot\text{CHCl}_2$ |                                                          |

The halogen atoms which are attached to the benzene ring are very firmly united, and are unable to enter into double decomposition reactions under the same conditions as aliphatic alkyl halides (for exceptions see p. 62); on the other hand, the halogen atoms of saturated side-chains react just like those in aliphatic compounds.

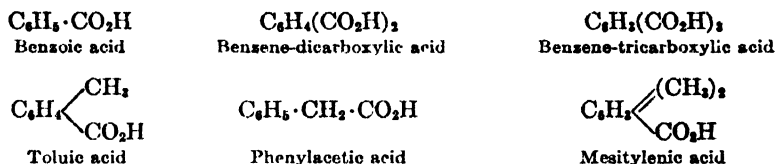
By the substitution of side-chain halogen by hydroxyl, the true alcohols of the benzene series are obtained:



The primary alcohols can be oxidised to aldehydes and acids:



Those acids in which the  $\text{CO}_2\text{H}$  is attached to the benzene ring can also be obtained by the direct introduction of carboxyl into benzene, or by the oxidation of homologous hydrocarbons of the benzene series:



In these acids, as well as in the alcohols and aldehydes, the hydrogen atoms of the benzene residue can be replaced by halogens,  $\text{NO}_2$ ,  $\text{SO}_2\text{H}$ ,  $\text{OH}$ , *etc.*

### General Properties of Aromatic Compounds

The principal differences between benzene and its derivatives on the one hand, and saturated aliphatic compounds on the other, as seen from the point of view of the preparative chemist, may be briefly summarised again, to show what is meant by "aromatic behaviour." They are:

1. Great ease of formation and stability of the benzene ring (see p. 26).
2. Hydrogen is more easily replaced when bound to a carbon atom in an aromatic compound than when linked to a carbon atom in an aliphatic compound. Substitution of hydrogen in the benzene nucleus succeeds under conditions where it would fail in the paraffin series.
3. Conversely, negative (p. 16) atoms such as the halogens, oxygen in the phenols, nitrogen in the aromatic amines and their derivatives, are more firmly bound than in the paraffin series.

The aromatic behaviour is not constitutionally related to the ring

structure as such, since cyclohexane and its derivatives do not show it; the latter behave like paraffins. The root of the aromatic properties must be the fact that each of the six carbon atoms in the benzene ring is linked with only three and not four atoms or groups.

According to *Kekulé's* formula, in which the six points of the hexagon are connected by alternate single and double bonds, benzene and its derivatives should be compared with olefins rather than with paraffins. Halogen atoms attached to an olefinic double bond, as in vinyl bromide,  $\text{CH}_2\text{:CHBr}$ , are, indeed, nearly as firmly linked as in the benzene nucleus. The acid properties of the phenolic hydroxyl group are comparable with those of the enols, and not with those of the alcohols. A more general discussion of the nature of the unsaturation of benzene is given later (p. 18). From the practical point of view the differences between the two series outweigh the analogies. The dominating feature of the olefins is addition, not substitution. The olefinic double bond is, in addition, a favoured point of attack in oxidation, whereas when benzene derivatives with saturated side-chains are oxidised the contrary is usually observed; the side-chain is destroyed, while the benzene ring remains intact.

### Isomerism of Benzene Derivatives\*

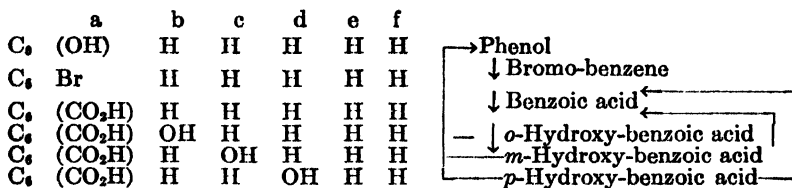
#### Proof of the Equivalence of the Six Hydrogen Atoms of Benzene.

If in benzene a hydrogen atom is replaced by another atom or group the product is a single compound, and isomeric mono-substituted compounds do not exist. There is only one chlorobenzene, one nitrobenzene, one aniline, one toluene, one benzoic acid, *etc.* Just as the four hydrogen atoms of methane are equivalent (Vol. I) so also are the six hydrogen atoms of benzene. Benzene has a symmetrical structure.

*History.*—*W. Körner* (*Giornale di Scienze Naturale ed Economiche*, Vol. V) and *A. Ladenburg* (*Ber.* 2, 274; 7, 1784; 8, 1666) proved the equivalence of the six hydrogen atoms of benzene simultaneously and independently, in 1869.

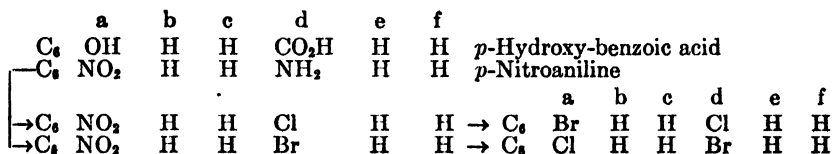
1. Both scientists used the conversion of the three mono-hydroxy-benzoic acids into one and the same phenol, as a proof of the equivalence of the three positions in the benzene ring occupied by these carboxyl groups. In addition, *Körner* reduced the three mono-chlorobenzoic acids with sodium amalgam to one and the same benzoic acid.

*Ladenburg* deduced the equivalence of a fourth hydrogen atom from the conversion of phenol into bromo-benzene, and further into benzoic acid. His proof of the equivalence of four hydrogen atoms in benzene is illustrated by the scheme:



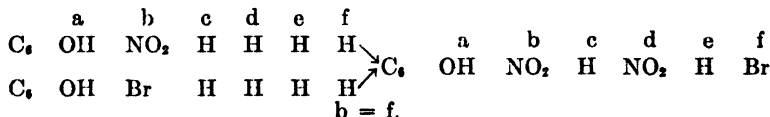
\* *A. Ladenburg*, *Theorie der aromatischen Verbindungen*, 1876.

*Körner* deduced the equivalence of the fourth hydrogen atom with the three hydrogen atoms replaced by carboxyl in the three mono-hydroxy- and the three monochlorobenzoic acids from the following facts: *p*-hydroxy-benzoic acid corresponds to *p*-nitraniline (*Arppe*), which can be converted either into *p*-nitrochloro- or *p*-nitrobromo-benzene. *p*-Nitrochloro-benzene, by replacement of the nitro-group by Br gives the same *p*-bromochloro-benzene as is obtained by substituting Cl for the nitro-group in *p*-nitrobromo-benzene. Hence the two H atoms which are replaced in *p*-nitraniline by the nitro and amino group, respectively, are equivalent, as are also the H atoms replaced by hydroxyl and carboxyl, respectively, in *p*-hydroxy-benzoic acid:



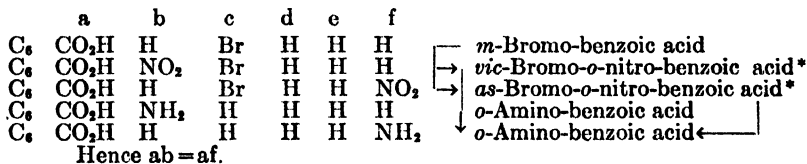
This proves the equivalence of four hydrogen atoms in benzene.

2. There are, with respect to each hydrogen atom in benzene, two pairs of hydrogen atoms in symmetrical positions, and the substitution of either atom of a pair by the same atom or group of atoms leads to the same compound. *Körner* proved this symmetry for two hydrogen atoms as follows: the same bromo-nitro-*o*-nitro-phenol is obtained either from that nitrophenol which is volatile and can be converted into catechol, and therefore belongs to the same series as salicylic acid, by replacing two hydrogen atoms by one bromine atom and one nitro group, or from *o*-bromophenol by introducing two nitro groups:



Consequently there are in phenol two hydrogen atoms in symmetrical positions to the hydroxyl group, and it makes no difference which of them is replaced by bromine and which by the nitro group. Now if this is true of one pair of hydrogen atoms, it must be true of the other pair also, since the symmetry of the first pair is impossible without that of the second. Therefore all the hydrogen atoms of benzene are equivalent.

The presence of two symmetrical pairs of hydrogen atoms in benzene can also be proved in the following way. The two different nitro-bromo-benzoic acids obtained by the nitration of *m*-bromobenzoic acid give the same *o*-amino-benzoic acid (*Hübner, Petermann, Ann.* 149, 129; 222, 111; *Ladenburg, Ber.* 2, 140):

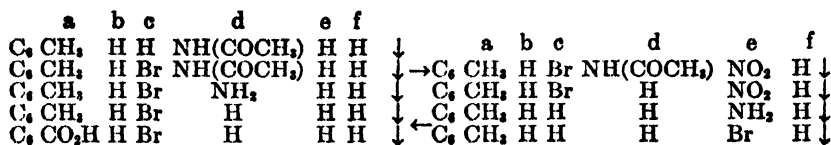


Therefore ab = af, and b = f

The symmetry of the second pair is shown (*Wroblevsky, Ann.* 192, 213; 234, 154) by the fact that the same *m*-bromotoluene is obtained from two bromine compounds in which Br replaces different hydrogen atoms, and therefore occupies symmetrical positions to the hydrogen atom replaced in toluene by methyl: ac = ae.

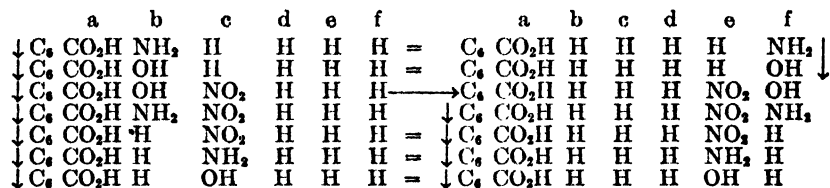
\* For the significance of the indices *vic*- and *as*- see the tri-derivatives, p. 14.





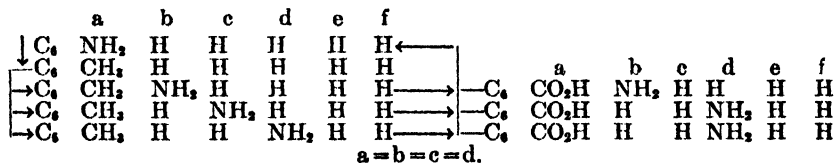
When this bromotoluene is oxidised, the same *m*-bromobenzoic acid is formed which *Hübner* and *Petermann* used as the starting material for preparing *vic*- and *as-m*-bromo-*o*-nitro-benzoic acid. It follows that bromine in the second experiment and the amino group of the *o*-amino-benzoic acid in the first replace different hydrogen atoms. Hence in benzene there is not only one, but two pairs of hydrogen atoms, which are symmetrical with respect to a fifth hydrogen atom. The equivalence of the six hydrogen atoms of benzene is thus proved (*cf. Ladenburg, Ber. 10, 1218*).

There is still another way of proving the symmetry of a second pair of hydrogen atoms, once the symmetry of the first pair is established. *o*-Aminobenzoic acid, obtained by the two methods indicated above, can be converted into the same salicylic acid, a hydroxy-benzoic acid. If this is nitrated, two different mononitro-salicylic acids are obtained. By heating the ethyl ethers of these two nitro-salicylic acids with ammonia, the ethoxyl groups can be replaced by the amido groups. From the nitramino-benzoic amides the free nitramino-benzoic acids can be obtained, and these are converted by nitrous acid and alcohol into one and the same nitro-benzoic acid. This nitro-benzoic acid prepared from either of the two different nitro-salicylic acids gives an amino-benzoic acid (*meta*) which is different from the acid originally used as the starting material for salicylic acid, and which can be converted into a hydroxy-benzoic acid (*meta*) not identical with salicylic acid. Therefore, two more hydrogen atoms in benzene occupy symmetrical positions to the one which is replaced by the CO<sub>2</sub>H-group:



There remains only one position for the hydroxyl group in the third hydroxy-benzoic acid, the *para*-position. There is only one possible *para*-position in benzene.

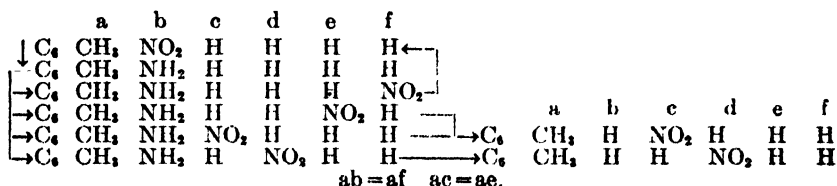
A very simple proof of the equivalence of the six hydrogen atoms in benzene has been given by *Noelting* (*Ber. 37, 1027*):



In amino-benzene, or aniline, the amino group is readily replaced by bromine and this by the CH<sub>3</sub> group by means of methyl iodide and sodium. In the toluene thus formed the methyl group occupies the same place as the amino group does in aniline. On nitration, toluene gives three isomeric nitrotoluenes, and these on reduction give three toluidines, which by acetylation, oxidation, and elimination of the acetyl group can be converted into three different amino-benzoic acids. When these lose CO<sub>2</sub>, one and the same aminobenzene (aniline) is obtained from all three; it is identical with the starting material, and the equivalence of four hydrogen atoms is thus proved.

To prove the second proposition, that two hydrogen atoms are in symmetrical positions to each hydrogen atom, *Noelting* starts with one of the nitrotoluenes just

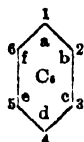
mentioned; here the  $\text{CH}_3$  group occupies position a. It is reduced to a toluidine, and from this, by the nitration of its acetyl compound and hydrolysis, four isomeric nitro-toluidines are obtained. Removal of the amino group from each of these gives four nitrotoluenes. Two of these are found to be identical with one another, and a third is identical with the nitrotoluene used as a starting material. Hence, the symmetrical positions of two pairs of hydrogen atoms is proved.



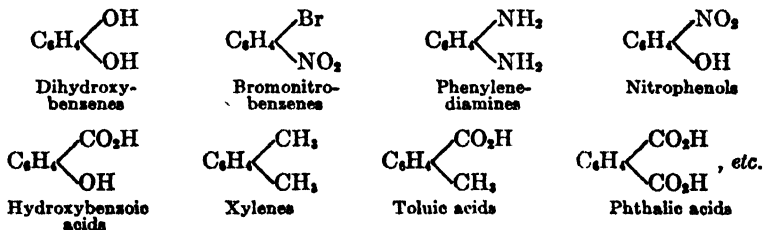
Therefore, the six hydrogen atoms of benzene are equivalent; two pairs of hydrogen atoms are symmetrically placed with respect to each hydrogen atom, and consequently, a di-substitution product of benzene can exist only in three modifications.

### Determination of the Positions of Substituents in Benzene Derivatives

The equivalence of the six hydrogen atoms of benzene is expressed by the hexagon formula. The way in which the carbon atoms forming the ring are united to one another will be discussed later. It is obvious that a di-derivative,  $\text{C}_6\text{H}_4\text{X}_2$ , obtained by substituting two hydrogen atoms,



can exist in three modifications, and that their isomerism is determined by the position relative to each other of the two groups which enter the ring. This kind of isomerism is called position isomerism (Vol. I). The three isomers are known for most of the disubstituted benzenes, and in no case are more than three isomers known. Thus, there are three:

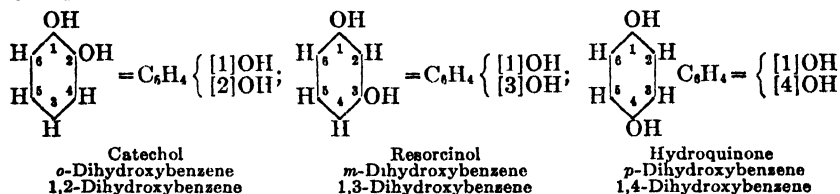


Each of the three isomers of these compounds can be converted into the corresponding isomer of the others. If, therefore, the relative positions of the substituting atoms or groups is known for the three isomers in one case, the configurations are known of all the other sets

of isomers into which the first set can be converted, provided the reactions used for the conversions do not involve any rearrangement of the groups in the molecule. For several disubstitution products the relative positions of the substituting groups have been established, *e.g.*, in the three dibromobenzenes, the three diaminobenzenes, and the three phthalic acids. These provide a basis upon which other disubstitution products can be arranged in three series, which are called the *ortho*-, the *meta*-, and the *para*-series.

In the *ortho*-compounds two adjacent hydrogen atoms of benzene are replaced. If the six hydrogen atoms are indicated by numbers, one of them being arbitrarily called 1, it is clear that there are two *ortho*-positions, the 1,2 and the 1,6, since positions 2 and 6 are symmetrical with respect to 1. The *meta*-compounds are obtained by substituting the hydrogen atoms 1,3 or 1,5. The 3 and 5 positions are symmetrical with respect to 1. The *para*-compounds are obtained when the hydrogen atoms 1 and 4 are replaced. Hence two equivalent positions 2 and 6 are available for *ortho*-substitution, and 3 and 5 for *meta*-substitution, but only one, *viz.*, 4 for *para*-substitution.

The relative positions of the substituting groups in di-derivatives are indicated either by prefixing *ortho*-, *meta*-, or *para*- to the name of the compound, abbreviated to *o*-, *m*-, and *p*-, respectively, or by prefixing the numbers, 1,2-, 1,3-, and 1,4-. In graphic formulae the benzene ring is written as a hexagon, and the atoms or groups attached to it are written at its corners. When writing ordinary formulae it is sometimes convenient to indicate the positions of substituting groups by numbers inserted between the benzene residue and the groups:

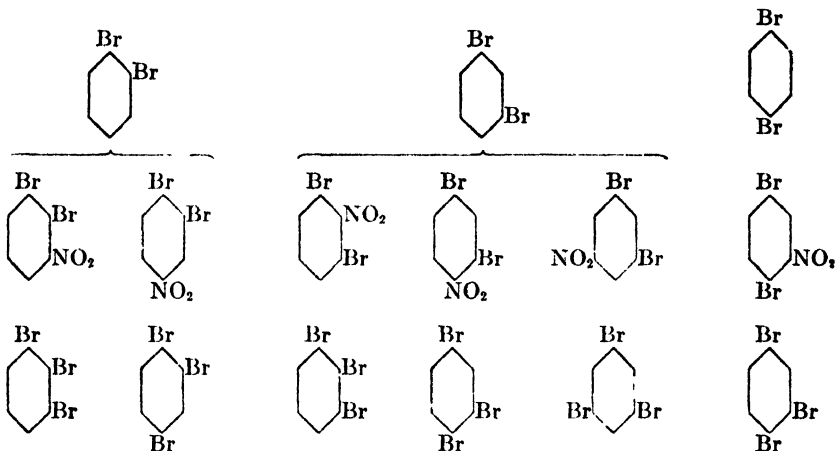


The following are important representatives of the three isomeric series:

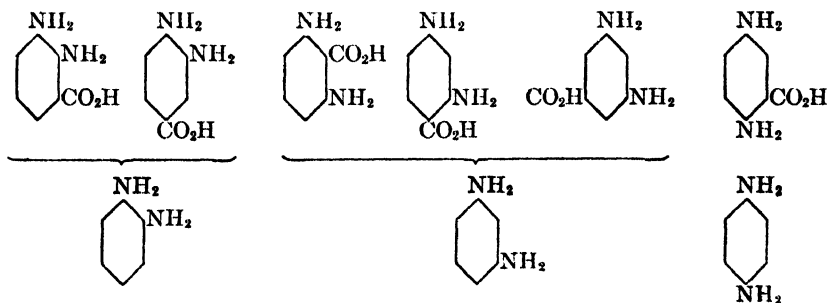
|                                                                                             | Ortho, 1,2       | Meta, 1,3                     | Para, 1,4                     |
|---------------------------------------------------------------------------------------------|------------------|-------------------------------|-------------------------------|
| $\text{C}_6\text{H}_4 \begin{cases} \text{OH} \\ \text{CO}_2\text{H} \end{cases}$           | Salicylic acid   | <i>m</i> -Hydroxybenzoic acid | <i>p</i> -Hydroxybenzoic acid |
| $\text{C}_6\text{H}_4 \begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$                 | <i>o</i> -Xylene | <i>m</i> -Xylene              | <i>p</i> -Xylene              |
| $\text{C}_6\text{H}_4 \begin{cases} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{cases}$ | Phthalic acid    | Isophthalic acid              | Terephthalic acid             |

**Determination of the Position of Substituents in di-Derivatives.** The hexagonal formula of benzene predicts two chemically identical *ortho*-, two chemically identical *meta*-, and one *para*-derivative, if the mode of linking of the six carbon atoms in the ring is disregarded for the moment.

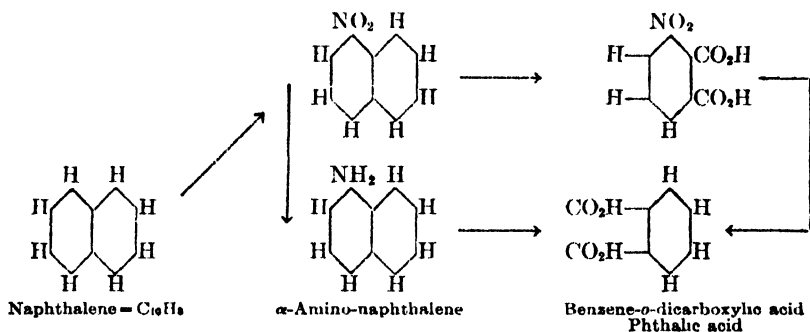
*Körner* was the first to indicate an experimental method for determining the positions of the substituents in the substitution products of benzene. He pointed out that a trihydroxybenzene which could be obtained from each of the three isomeric dihydroxybenzenes, all of which were known at the time, must necessarily be the 1,3,4-trihydroxybenzene (Bull. Acad. Roy. Belg. [2], 24, 166). As the conversion of dihydroxy- into trihydroxybenzene proved to be difficult, *Körner* (1874) used in their place the dibromobenzenes, and by converting them into tribromobenzenes established their absolute configurations (Gazz. 4, 305). He nitrated the three dibromobenzenes; the first gave two, the second three (p. 63) and the third one mono-nitro-dibromobenzene. He reduced the six mononitro-dibromobenzenes to monoamino-dibromobenzenes and converted the latter into the three tribromo-benzenes. *Körner* showed that by this sequence of reactions the first dibromobenzene gave two different tribromobenzenes, the second three, but the third only one. Assuming the hexagonal arrangement of atoms in benzene, *Körner* concluded that the first dibromobenzene had its two bromine atoms in the ortho-, the second in the meta-, and the third in the para-position. From this, the absolute configuration of the bromine atoms in the three tribromobenzenes and the constitution of the six mononitro-dibromobenzenes followed. The argument is illustrated by the following scheme, in which the H atoms and the double bonds are not shown:



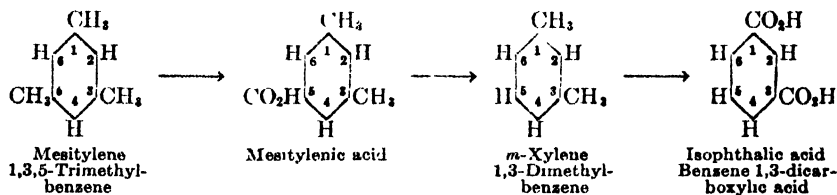
What may be described as the converse of this argument was used by *P. Griess* (Ber. 5, 192; 7, 1223) for the phenylene-diamines. There are six diaminobenzoic acids; two of these acids give the same phenylene-diamine on loss of  $\text{CO}_2$ ; this must be the ortho-compound. Another phenylene diamine is formed from three of the acids and must be the meta-compound, while the third phenylene diamine is obtained from only one of the acids, and hence must be the para-compound.



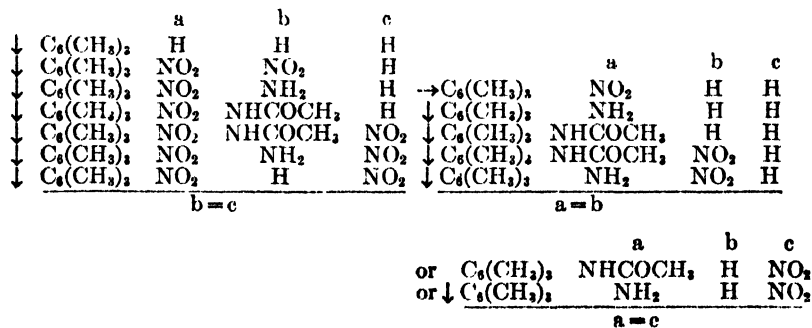
The configurations of benzene derivatives with side-chains were established by converting them into benzene-carboxylic acids. The configurations of the three benzene-dicarboxylic acids, or phthalic acids, were settled by *Graebe* (Ber. 4, 501) in the following way. The phthalic acid obtained by the oxidation of naphthalene is the 1,2- or *o*-benzene dicarboxylic acid, because naphthalene consists of two benzene rings which share two adjacent C atoms. On oxidation of nitro-naphthalene, nitro-*o*-phthalic acid is formed, which can be converted into phthalic acid; on oxidation of amino-naphthalene obtained by reduction of nitro-naphthalene, *o*-phthalic acid is formed. In the first case one of the benzene rings in naphthalene is destroyed by the oxidation, in the second the other. This proves the constitution of naphthalene, and at the same time phthalic acid is shown to be the *o*-dicarboxylic acid of benzene:



Isophthalic acid is benzene *m*-dicarboxylic acid, since it is the oxidation product of *m*-xylene; the latter is *m*-dimethyl benzene, as proved by its formation from mesitylenic acid, the first oxidation product of mesitylene or 1,3,5-trimethylbenzene:



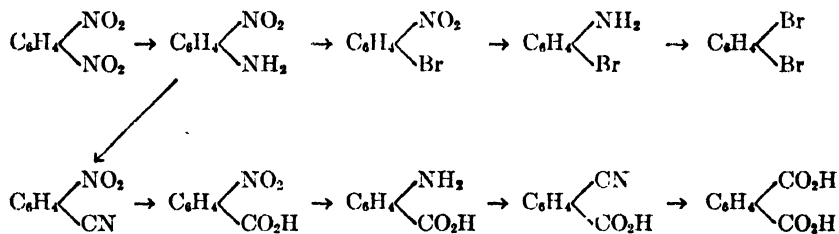
*Ladenburg* proved that mesitylene was 1,3,5-trimethylbenzene by showing that the three hydrogen atoms of mesitylene which are not replaced by methyl groups are all equivalent (Ann. 179, 174):



The course of the argument can be followed from the above scheme. Mesitylene gives dinitro-mesitylene, in which two hydrogen atoms, say, a and b, are replaced. This is successively converted into nitro-amino-, nitro-acetamino-dinitro-acetamino-, dinitro-amino-, and dinitro-mesitylene; the last is identical with the starting material, and therefore b and c are equivalent. The nitro-amino-mesitylene in which the amino-group is, say, in the position b, gives mononitro-, mono-amino-, mono-acetamino-, mono-acetamino-nitro-, and finally mono-amino-nitro-mesitylene, identical with the nitro-amino-mesitylene obtained in the first reduction of dinitro-mesitylene. Therefore a and b, or a and c, are equivalent; but b and c have been shown to be equivalent; hence the equivalence of the three hydrogen atoms of mesitylene which are not substituted by methyl is proved. Mesitylene must be symmetrical, and its methyl groups occupy the positions 1,3,5.

For the third benzene-dicarboxylic acid, terephthalic acid, there is only one possibility left. It must be the para-compound. This is confirmed by the following facts. Terephthalic acid is obtained from *p*-dimethyl-benzene, and this from *p*-bromotoluene by the action of methyl iodide and sodium. *p*-Bromotoluene gives *p*-bromobenzoic acid on oxidation. The latter belongs to the same class as *p*-hydroxybenzoic acid, since both are obtained from one and the same *p*-amino-benzoic acid by means of diazo-reactions. Now it has already been proved (p. 8) that in *p*-hydroxybenzoic acid the hydroxyl group has replaced a hydrogen atom which is not equivalent to any of the remaining four nuclear hydrogen atoms in benzoic acid.

The three phthalic acids can be related to the disubstitution products of benzene in which the substituents do not contain carbon. The three dinitrobenzenes can be converted into nitro-amino-, bromonitro-, bromo-amino-, and dibromobenzenes on the one hand, and into nitrocyano-, nitrocarboxylic-, aminocarboxylic-, cyanocarboxylic-, and phthalic acids on the other hand, and intramolecular rearrangement of substituents has never been observed in these reactions (*Sandmeyer*, Ber. 18, 1492, 1496):



A further proof is furnished by the derivatives of the three isomeric xylenes. *m*-Xylene gives three nitro-xylenes, three xylidenes, and three xylenols; *o*-xylene gives two compounds of each of these types, and *p*-xylene gives only one nitro-xylene. Hence it follows that *m*-xylene and isophthalic acid, its oxidation product, are the 1,3-compounds, *o*-xylene and phthalic acid the 1,2-compounds, and *p*-xylene and terephthalic acid the 1,4-compounds (*Noelting*, Ber. 18, 2687).

That in the ortho-compounds the substituents are, in fact, attached to two adjacent carbon atoms of the ring is further shown by the fact that with these compounds simple reactions often take place very readily in which the products contain a new ring formed by union of the substituents, and are carbocyclic or, more frequently, heterocyclic compounds. (see *o*-phenylene diamine, *o*-aminophenol, *o*-aminothiophenol, *o*-aminobenzaldehyde, *o*-phthalic acid, *o*-hydroxycinnamic acid, etc.). The conclusions drawn from these older arguments about the configurations of the substitution products of benzene are confirmed by the more recent crystallographic analysis of the molecular structure of certain of them, e.g., resorcinol (1,3-dihydroxybenzene) (*Robertson*, Proc. Roy. Soc. A 157, 79).

**Isomerism of the poly-Substitution Products of Benzene.** When three or more hydrogen atoms of benzene are replaced two cases must be distinguished: the substituents are either all the same or

different. In the first case compounds with three substituents, such as  $C_6H_3(CH_3)_3$ , can exist in three isomeric forms, with the substituents in the positions 1,2,3, 1,2,4, and 1,3,5. The isomers are best distinguished by prefixing these sets of numbers before the name, but an older method is to use the prefixes *vic* (= vicinal), *as* (= asymmetric) and *s* or *sym* (= symmetrical) for the three isomers. In tetrasubstituted compounds with four identical substituents there are again three possibilities: 1,2,3,4, 1,2,4,5, and 1,2,3,5.

With five or six identical substituents only one modification is possible: there is one pentachlorobenzene,  $C_6HCl_5$ , and one hexachlorobenzene,  $C_6Cl_6$ .

If the substituent groups are not identical, the number of possible isomers is much greater. It can easily be deduced from the hexagonal structure. Thus the formula for dinitrobenzoic acid,  $C_6H_3(NO_2)_2COOH$ , requires the existence of six isomers: 1,2,3, 1,2,4, 1,2,5, 1,2,6, 1,3,4, and 1,3,5, where the carboxyl group is assigned the position 1.

The constitution of benzene poly-substitution products is deduced from their relationship to di-substitution products of known structure.

### Substitution Rules

**Formation of di-Substitution Products.** When benzene or toluene is chlorinated or brominated and when the mono-halogeno-benzenes are nitrated or sulphonated, the products are almost entirely the *para*- and *ortho*-compounds; when, on the other hand, benzene or nitrobenzene is nitrated energetically, *m*-dinitrobenzene is the principal product. Phenol and aniline behave like toluene, giving *p*- and *o*-di-derivatives, while *m*-compounds are the chief products from benzenesulphonic acid,  $C_6H_5SO_3H$ , benzoic acid,  $C_6H_5COOH$ , benzaldehyde,  $C_6H_5CHO$ , benzonitrile,  $C_6H_5CN$ , acetophenone,  $C_6H_5COCH_3$ , and other compounds with an acyl group attached to the benzene ring. As can be seen from these examples the substituent already present in the ring exerts a controlling influence on the position at which subsequent substitution takes place. The nature of the entering group, the new substituent, is of no importance; the position it takes up is determined by the nature of the group already attached to the ring. Chlorobenzene gives on nitration chiefly *p*-nitrochlorobenzene, but nitrobenzene on chlorination gives mainly *m*-nitrochlorobenzene. The first substituent obviously exerts a selective influence on the non-substituted positions. According to the nature of this influence substituents are classified as of the first or second class.

1. Substituents of the first class usually facilitate substitution in the *ortho*- and *para*-positions (exceptions, see p. 22). They direct to these positions and substitution is easier than in benzene itself. Alkyl groups, the halogens, OH, OR,  $NH_2$ ,  $NR_2$ , SR, *etc.*, are substituents of the first class.

2. Substituents of the second class hinder substitution in the *ortho*- and *para*-positions. They direct to the *meta*-position and

make substitution, in general, more difficult. Such substituents are  $\text{NO}_2$ ,  $\text{COOH}$ ,  $\text{CN}$ ,  $\text{CHO}$ ,  $\text{COR}$ ,  $\text{SO}_2\text{OH}$ ,  $\text{SO}_2\text{R}$ , etc.

The reasons underlying these simple generalisations, which cover the greater part of all that has been observed in benzene substitution, are bound up with the nature of the benzene ring itself, and are more easily discussed in a later section (p. 21). Before these reasons were understood various rules were proposed which attempted to summarise the allotment of the various groups to the two classes, and to link up that allotment with some other property of the groups. These rules are nowadays only of historical interest, since it is now clear that the phenomena are more complex than can be compressed into a simple rule. Examples of such rules are:

*Crum Brown and Gibson's rule:* If the hydrogen compound of the atom or radical which forms the substituent already present can be oxidised directly, i.e., in one operation, to the corresponding hydroxy-compound, then, on substitution, ortho- and para-derivatives will be formed; otherwise meta-derivatives (J. 1892, 61, 367).

*Hammick and Illingworth's rule* (J. 1930, 2358): If, in the benzene derivative  $\text{C}_6\text{H}_5\text{XY}$ , Y is in a higher group of the periodic table than X, or if, being in the same group, Y is of lower atomic weight than X, then XY is a substituent of the second class. All other substituents, including single atoms, are of the first class.

*Vorländer's rule* (Ber. 52, 268) is of the same type as that of *Hammick*, and both break down in certain cases.

While the generalisations given above apply to the main product formed in substitution reactions, it must be remembered that in all cases all three isomers are formed, but usually one or two of them in small proportion. This proportion is often so small that the presence of the isomer can only be established by special methods. The most valuable contributions to our knowledge in this field were made by *Holleman* and his school.

All that has been said so far applies to the ordinary reactions which are described as substitution reactions, i.e., nitration, halogenation, sulphonation, and the coupling reaction of amines and phenols with aromatic diazo compounds. In certain less common reactions, however, the directing effect of groups attached to the ring is the opposite to that given above; for example, when nitrobenzene is heated with caustic potash the product is *o*-nitrophenol and not the meta-compound (*Wohl*, Ber. 32, 3486; 34, 2444). Substituting reagents can, in fact, be divided into two classes; one of these includes the more common reagents, such as  $\text{HNO}_3$ ,  $\text{Br}_2$ ,  $\text{H}_2\text{SO}_4$ , and these are called cationoid reagents because they resemble active cations or are indeed cations, such as  $\text{PhN}_2^+$ , and the other the anionoid class, contains the active anions, such as  $\text{OH}^-$  and  $\text{CN}^-$ . The reasons for the difference in place of attack of these two classes is given in greater detail on p. 22.

**Formation of tri-Derivatives.** When a di-derivative is further substituted, the directing effects of the two existing substituents are superimposed (see *Holleman*, "Die direkte Einführung von Substituenten in den Benzolkern," Veit, Leipzig). In 1,2- and 1,4-derivatives, one substituent of the first and one of the second class combine to direct a third substituent into the *o*- and *p*-positions with



respect to the first, and into the *m*-position with respect to the second; from the 1,4-di-derivative the 1,2,4-tri-derivative is formed almost exclusively, while from the 1,2-di-derivative the 1,2,4-, and, in some cases, the 1,2,6-tri-derivative is formed. When, on the other hand, both substituents in an *o*- or *p*-derivative are of the first class, their directing influences act in opposite directions, and the effect of the stronger predominates. The strongest groups directing into *o*- and *p*- are OH and NH<sub>2</sub>, the halogens are weaker, and the alkyl groups weakest. In meta-di-derivatives substituents of the same class act together. If of the first class they join forces to direct to positions 2, 4, or 6, and several position isomeric tri-derivatives are formed. If they are of the second class, they direct jointly to the 5 position, and the symmetrical 1,3,5-derivative is the only product.

**Formation of tetra-Derivatives.** With three substituents attached to the ring, the superimposition of their directing effects can, of course, lead to more complicated results. The importance of the strength of a directing group is shown in a simple example. When phenol is vigorously nitrated 2,4,6-trinitrophenol is formed, owing to the combined *o*- and *p*-directive influence of the hydroxyl group and the *m*-directive effect of the nitro-groups which first enter. When phenol or aniline is brominated the bromine atoms which enter direct to *o*- and *p*-positions relative to themselves, that is to say, to the 3 and 5 positions, and yet 2,4,6-tribromophenol or -aniline is formed owing to the dominating influence of the strong OH or NH<sub>2</sub> groups.

### Structure of the Benzene Nucleus\*

*Kekulé's* benzene theory involved the assumption that the benzene molecule contains six carbon atoms linked together to form a regular hexagon. This assumption found full support from the chemical evidence which has been given above and of which the more important parts are the correct prediction of the number of isomeric substitution products and the demonstration of the equivalence of the six hydrogen atoms in the benzene molecule. That a six-membered ring is present was shown later by the conversion of benzene into cyclohexane and the converse transformation, an example being the experiments of *Willstätter* and *Hatt* (Ber. 45, 1464) in which cyclohexanol was subjected to operations which introduce a double bond into the ring: after three such steps the product was benzene; this evidence is, of course, no support for the assumption that the hexagon is regular.

What was clearly needed next was some explanation of the way in which the six carbon atoms are united to one another, and this remained for many years the great problem. *Kekulé* postulated alternate double and single bonds between the atoms, so that each atom

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\* Because of the recent profound change in outlook on this classical problem of organic chemistry, I have found it necessary to rewrite the whole of this section myself. T. W. J. T.

was shown as tetravalent, and this was undoubtedly the best assumption that could be made at the time, and it could be extended to all the other known aromatic systems such as the polycyclic compounds (naphthalene, phenanthrene, *etc.*) and the heterocyclic aromatic compounds (pyridine, quinoline, *etc.*). It was, however, by no means satisfactory. As has been pointed out already, benzene does not show the same kind of unsaturation that is typical of double bonds in the olefins; it is unsaturated, since it can be reduced on active catalysts to cyclohexane, it will take up chlorine or bromine to form hexahalides, but only when the halogen has been activated by illumination, and it will combine with ozone, but the sluggishness of these addition reactions, and, above all, its great resistance to oxidation, show that if benzene is said to contain three double bonds, they must be assigned quite different properties from those in olefinic compounds. A further difficulty was that this postulate in its simple form does not account for the equivalence of the hydrogen atoms in benzene; in fact, it does not imply that the hexagon is regular. At its face value it implies that there should be two different ortho-derivatives, the 1,2 and the 1,6 compounds, in one of which the two carbon atoms carrying substituents are united by a single bond, and in the other by a double bond. *Kekulé* overcame this second difficulty by the assumption that in some way the double bonds oscillated so that their exact position could not be defined, but this was in itself as assumption of an entirely different and new kind for which no direct experimental evidence could at that time be put forward.

These difficulties led to a large number of new proposals for the structure of the benzene nucleus. None of these was satisfactory or received universal consent, and the reason lay in the fact that at that time there was not, on the one hand, sufficient theoretical knowledge of the mechanism of the linking of atoms, nor, on the other, had experimental methods been developed which could throw new light into the dark recesses of the problem of aromatic structure in general.

There is no need to discuss these proposals in any detail. They can be divided into two classes. In the first, the hexagonal structure of the benzene molecule was thrown overboard and other possibilities advanced: an example is the triangular prism model of *Ladenburg* (Ber. 2, 141, 272). Since nowadays we have direct and overwhelming evidence of the truth of the regular hexagonal structure, such proposals have only a historical interest. In the second class the hexagonal structure was retained and the proposals were restricted to the method of linking between the six carbon atoms. Some of them were valuable in that they emphasised points of analogy between the aromatic compounds and certain types of non-aromatic compounds: an example is a paper by *Thiele* (Ann. 306, 125) of which the essence can be put as follows. An aliphatic chain consisting of alternate single and double bonds (a "conjugated" system) is known to exhibit certain properties not normal to isolated double bonds, or to double bonds separated by more than one single bond; now benzene on the *Kekulé* formula is such a system with the addition that the chain is joined up to make a ring, and thus the conjugation extends

all round the ring (a "closed conjugated system"). Hence it is not surprising that the double bonds of *Kekulé's* postulate do not behave like ordinary isolated double bonds. Other suggestions of this class were not so illuminating; examples are the centric formula of *Claus* (*Theoretische Betrachtungen und deren Anwendungen zur Systematik der organischen Chemie*, Freiburg, 1867) and that suggested by *Armstrong* (*J.* 51, 264, footnote) and supported by *Baeyer* (e.g., *Ann.* 269, 188). In such proposals formulae were advanced in which one of the four valencies of each of the carbon atoms was shown linked in a manner entirely different from that used in the formulation of any other compound. Such formulae were in reality little more than a confession that the problem remained unsolved; a valency bond drawn between two atoms had a precise significance, but a valency bond drawn towards the centre of a hexagon implied nothing precise, but was only a visual presentation of the fact that with the knowledge then available no further progress could be made. It may be said that some of these proposals, and especially that of *Thiele*, contained the germ of what we consider today to be the solution of the problem. This is true much to the same extent that certain of the ancient Greek philosophers can be given the credit of establishing the atomic theory of matter. In both instances there was an urgent problem and during its discussion many suggestions were put forward, and some of these were rudimentary forms of what was later held to be the solution; but in neither case was there sufficient practical or theoretical knowledge for accurate discrimination between the alternatives.

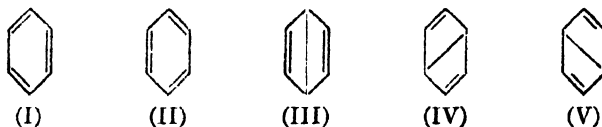
The most important advance in experimental knowledge which has removed most uncertainty in the problem of the structure of benzene and the other aromatic compounds is the development of methods by which the positions of atoms in a molecule and the distances between them can be measured with high accuracy. These methods are of very different types, the most important being the full analysis of the crystalline structure of compounds in the solid state by the observed diffraction of X-rays, the diffraction of electrons by compounds in the gaseous state, and the interpretation of the band spectra of molecules; they have survived rigid testing and the results they give are in close agreement. The knowledge derived from these methods removes much uncertainty in the problem: the actual shape of the whole of the benzene molecule is now known with high accuracy, and some of the earlier suggestions can be ruled out without any hesitation. Further, it is now realised that the distance between two atoms which are chemically linked is of great importance for disclosing the nature of the link. Hence the results of these methods are direct evidence that the link which joins the carbon atoms in benzene is not identical either with the single C—C link in ethane, or with the link C=C in ethylene. The existence of a link different from either of these had not, of course, been established in *Kekulé's* time.

More important, perhaps, has been the advance on the theoretical side. There is now some knowledge of the mechanism of chemical

linking; the union of two atoms by a chemical bond is known to be due to the interaction of the valency electrons of the atoms, and the types of interaction are known, and the quantitative laws which govern it are known to be those of the general system of quantum mechanics. It had been realised for many years that a chemical link had something to do with the valency electrons and electronic formulae for benzene had been put forward, *e.g.*, by *J. J. Thomson* (*Phil. Mag.* 1914, 27, 784), but until comparatively recently such formulae had no real significance because the quantitative laws governing the interaction were unknown. It is impossible to summarise in this place the present state of knowledge in this field; the reader can be referred to the simple and clear account of the subject given by *Pauling* in his book, "The Nature of the Chemical Bond" (Cornell University Press, 1939). One general principle emerging from quantum mechanics is, however, of great importance for the immediate purpose, and must be mentioned here. This is the concept of resonance, which was first introduced by *Heisenberg* in 1926 (*Z. Physik*, 39, 499). This concept, which is a necessary consequence of the laws of quantum mechanics, is an addition of an entirely new kind to the classical theories of valency and provides the solution to the benzene problem. The reason why that problem remained unsolved for so long was because the classical theories, without this addition, were completely incapable of dealing with it. The principle of resonance (also called mesomerism) can be put into words as follows: If there is a molecule for which two or more formulae can be written, and the structures implied by the formulae do not differ much in energy content and not at all in the relative positions of the atomic nuclei but only in the positions of their electrons, then the actual structure of the molecule will not be any one of the formulae which can be written, but will be a "mixture" of all the possible structures, and, most important of all, its energy content will be smaller than that of any of the structures which can be thought of as contributing to the actual structure. Such a molecule can be described as a resonance-hybrid, and it will be more stable than any of the structures written because of this lower energy content. A substance composed of molecules of this kind must not be thought of as being a mixture of different kinds of molecules; such mixtures are known and this phenomenon is tautomerism. With a resonance hybrid all the molecules are alike and it is impossible to represent them by one single formula if the classical symbols are used. The existence of resonance in any given case can sometimes be inferred from the properties and stability of the compound, but is best established by quantitative measurement of the energy of the molecule, a lower energy than that expected indicating resonance directly, or by measuring the distances between the atomic centres in the molecule. The lengths of many normal bonds are known with accuracy; in most resonance hybrids the bonds are not normal, but hybrids between bonds of various kinds. It is known experimentally that the lengths of hybrid bonds are intermediate between those of the bonds of which they are compounded. Hence, measurements of

bond length and its comparison with the known normal lengths disclose the hybrid nature of the bond.

The shape and size of the benzene ring are known with high accuracy from the study of the electron diffraction of benzene vapour (*Pauling and Brockway*, J. Chem. Phys. 2, 867), from the X-ray diffraction of many crystalline benzene derivatives (see e.g., *Robertson and Woodward*, Proc. Roy. Soc. A 162, 568; J. 1937, 219), and from extensive spectroscopic investigation of benzene and all the possible compounds obtained by substituting deuterium for hydrogen in benzene (for references see Ann. Rep. Chem. Soc. 1938, 34, 200). It is a regular plane hexagon, and the length of each side is  $1.390 \pm 0.005$  Å. The distance between linked carbon atoms in all the paraffins and cycloparaffins, and also in the diamond, is 1.54 Å., and between doubly bound carbon atoms in ethylene and its derivatives is 1.34 Å. Hence the six bonds of the benzene ring are all alike and are hybrids in which double and single bonds are the main components. The benzene ring is thus a resonance hybrid and no single classical formula can be written to represent it. This conclusion is obvious once the existence of resonance has been realised. Using the classical symbols we can write for benzene two Kekulé formulae (I and II) and three Dewar formulae (III, IV, and V). The first



two will have exactly the same energy, and hence there must be resonance between them, and the last three will have a higher energy, but must contribute to a small extent to the molecule which is a resonance hybrid. A further necessary consequence is that the energy content of the actual molecule must be lower than that of the component structures: the actual molecule must have a smaller energy content than the two Kekulé structures (I and II) and hence be more stable than them. This is the explanation of the fact, so puzzling on the older view, that benzene is so stable in spite of its apparently unsaturated nature. This point is best shown by the quantitative measurements of the heat evolved on reduction of double bonds in various compounds (*Kistiakowsky* and co-workers, Am. 57, 65, 876; 58, 137, 146; 59, 831). The data important for the present purpose are given in the table on page 21.

From these it can be seen that in the olefins (one double bond) the heat effect is much the same, though substitution of hydrogen atoms on the doubly bound carbon atoms by alkyl residues reduces it by 2-3 kg.-cals. Cyclohexene has the same value as *cis*- $\Delta^3$ -butene in which the double bond is similarly situated. With two double bonds in a chain the heat is twice that for one double bond if the double bonds are not conjugated (comparison of  $\Delta^{1,4}$  penta-diene with  $\Delta^1$ -butene). If they are conjugated, as in butadiene, the

heat effect is 3.6 kg.-cals. less; in other words, the molecule contains this amount of energy less, and can be said to be stabilised to this extent. This is the resonance stabilisation of conjugated double bonds. Cyclohexadiene with conjugated double bonds is the same as the aliphatic conjugated compound if allowance is made for the substitution. Benzene, however, is completely different; if it is

HEAT EVOLVED (KG.-CAL.) ON ADDITION OF HYDROGEN TO 1 GM. MOL. AT 82°

| <i>Addition of H<sub>2</sub></i>  |                                                         |              |
|-----------------------------------|---------------------------------------------------------|--------------|
| Ethylene                          | CH <sub>2</sub> :CH <sub>2</sub>                        | 32.58 ± 0.05 |
| Δ <sup>1</sup> -Butene            | CH <sub>2</sub> :CH·CH <sub>2</sub> Me                  | 30.34 ± 0.06 |
| cis-Δ <sup>2</sup> -Butene        | CHMe:CHMe                                               | 28.57 ± 0.06 |
| Cyclohexene                       |                                                         | 28.59 ± 0.10 |
| <i>Addition of 2H<sub>2</sub></i> |                                                         |              |
| Δ <sup>1,4</sup> -Pentadiene      | CH <sub>2</sub> :CH·CH <sub>2</sub> ·CH:CH <sub>2</sub> | 60.79 ± 0.15 |
| Δ <sup>1,3</sup> -Butadiene       | CH <sub>2</sub> :CH·CH:CH <sub>2</sub>                  | 57.07 ± 0.15 |
| Δ <sup>1,3</sup> -Cyclohexadiene  | CH:CH·CH:CH<br>└──(CH <sub>2</sub> ) <sub>2</sub> ──┘   | 55.37 ± 0.10 |
| <i>Addition of 3H<sub>2</sub></i> |                                                         |              |
| Benzene                           |                                                         | 49.80 ± 0.15 |

allotted three double bonds (Kekulé formula) the heat of hydrogenation should be three times that of cyclohexane, *i.e.*, 85.77 kg.-cals., while it is in fact 36 kg.-cals. less than this. This is the clearest experimental demonstration of the truth of the resonance stabilisation of a molecule such as benzene. The results can be used in another way. By subtraction we can find the energy change on hydrogenating benzene in stages to cyclohexane.

|                              |                                   |
|------------------------------|-----------------------------------|
| Benzene → cyclohexadiene     | + 5.66 kg.-cals. energy absorbed. |
| Cyclohexadiene → cyclohexene | - 26.8 kg.-cals. energy evolved.  |
| Cyclohexene → cyclohexane    | - 28.6 kg.-cals. energy evolved.  |

The endothermic first stage shows the high stability of the benzene system in which there is resonance between two structures of identical energy. Considerations similar to these can be used in all aromatic systems (see *Pauling, op. cit.*) and it can be said that the problem of the structure of benzene has been solved.

### *Substitution in the Benzene Nucleus*

There remains the question of the reasons for the substitution phenomena which have been described above. Here there has also been much advance and the main parts of the problem can be regarded as settled, although there is not the quantitative knowledge which is available in the case of the problem just discussed. The advances have been due to the work of many, including *Robinson, Ingold, Lapworth, and Lucas.\**

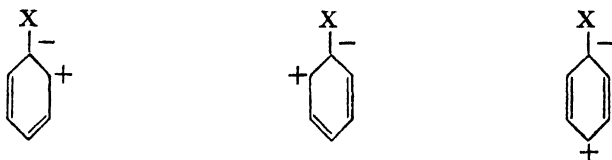
\* For fuller discussion see *H. B. Watson, "Modern Theories of Organic Chemistry,"* Oxford, 1937, p. 45 *et seq.*

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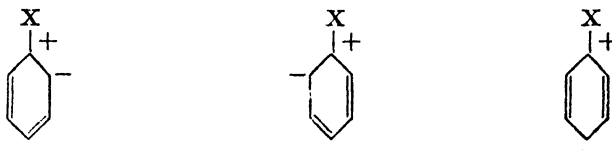
The first point now realised is that substituting reagents must be divided into two classes (*Robinson*, "Outline of an Electrochemical Theory of the Course of Organic Reactions," Inst. of Chemistry, London, 1932). The first class includes those reagents encountered in the more usual substitution reactions, and are those dealt with in the classical orientation rules. It contains reactive cations, such as the diazonium ion in coupling reactions (p. 125), acids such as nitric and sulphuric acids, the halogens and the alkyl halides. These are called cationoid (electrophilic) reagents, and the common term between them is that the radical which becomes attached to the ring is either a cation or approximates to a cation in that the other radical with which in combination it forms the substituting reagent is an anion or tends to be. Thus, with bromine the other product of substitution is HBr in which the bromine is an anion; hence the bromine which has entered the ring is cationoid. The second class of substituting reagents is the anionoid class, where the actual reagent is an anion, such as  $\text{OH}^-$  and  $\text{CN}^-$ ; with these, as has been pointed out above (p. 20), the converse of the classical orientation holds. From this classification it is clear that cationoid reagents will attack the benzene ring at a point where there is an excess of electrons, their positive charge, or potential positive charge being attracted by the negative charge. Similarly anionoid reagents will attack at a place where there is a deficiency of electrons, and hence cannot substitute in the same position as cationoid reagents.

The next point is the reason for the existence of excesses and deficiencies of electrons in the various positions of the benzene ring, and since the position of substitution depends only on the nature of the group already attached to the ring, the reason must lie in interactions between these groups and the electrons of the ring. The interactions are of two different kinds, and it is because there are two competing effects that the actual observed phenomena are so complex and difficult to frame in an all-embracing rule. The existence of the two kinds of effect is known from extensive observation of the course of reactions and of the physico-chemical properties of compounds, such as the strengths of acids and bases (see *Watson*, *op. cit.*) and has been verified by quantum-mechanical calculation (*Hückel*, *Z. f. Physik* 1931, 72, 310; *Pauling* and *Wieland*, *Am.* 57, 2086).

The first kind of effect is called the inductive effect. It arises from the electron-repelling or electron-attracting power of the group attached to the ring. The two extreme cases of this effect are when the group is actually carrying a negative or positive charge. If the attached group is the ion  $\text{NMe}_3^+$ , this will alter the distribution of electrons in the ring so that they move towards the ammonium group and the nuclear carbon atom to which it is united. Because of the structure of the ring the carbon atoms in the ortho- and para-positions will have an electron density lower than that in benzene as a whole; this follows from the possible structures which can contribute to the resonance hybrid. The only charged structures that can be written are:



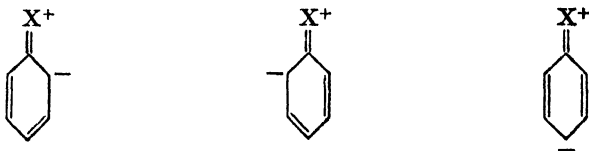
Hence the actual structure will contain these as components and the para and two ortho atoms will not be positions for attack by cationoid reagents. Such groups will be meta-directing and the reactivity will be lowered even in the meta-position by the electron-attracting group attached. In the converse case, take a compound such as sodium benzoate; the attached group,  $\text{—COO}^-$ , is an anion, and is electron-repelling. Here the carbon atoms in the ortho- and para-positions will have an electron density greater than in benzene, but not the meta atoms. This is again because the only possible structures which contribute to the actual structure are:



Hence with cationoid reagents the group is ortho-para-directing, and because of the increased electronic density in these positions substitution takes place more easily than with benzene itself.

It should be noticed that the uncharged amino group  $\text{—NR}_2$ , and the uncharged carboxyl group  $\text{—COOH}$  have directing effects opposite to those which they show when ions. This striking fact discloses the nature of the process. All groups must exercise an inductive effect: the methyl group is electron-repelling and hence with cationoid reagents is ortho-para-directing.

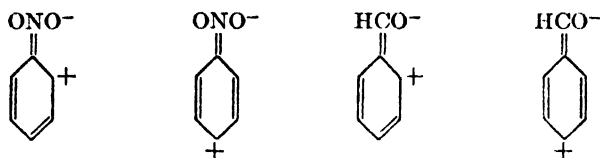
The inductive effect alone cannot explain the observed phenomena. If it were the sole effect it would be impossible to understand the ortho-para-directing powers of groups such as  $\text{—Cl}$ ,  $\text{—Br}$ , and  $\text{—OH}$ ; all these are known to attract electrons from measurements of electric moments and hence their inductive effect would put them in the same class as  $\text{—NR}_2^+$ , and they would be meta-directing. There is a second effect for which we have experimental evidence, mentioned below. This is the electromeric effect, also called the resonance effect or the tautomeric effect, though the two latter terms are unfortunate in this connexion. If the atom attached to the ring in the directing group contains unshared electrons, in addition to the usual possible component structures for the benzene ring there are three others:





These must form part of the resonance hybrid and hence in the actual structure the electron density is high in the ortho- and para-positions, and groups of this kind are ortho-para-directing with cationoid reagents, and unless the inductive effect working in the opposite direction is strong, the compounds are much activated for substitution. Examples are the rapid substitution with  $\text{—OH}$  or  $\text{—NH}_2$  as directing group. The competition between the two effects is shown with  $\text{—Cl}$  or  $\text{—Br}$ , which are ortho-para-directing, but not so strongly as with  $\text{—OH}$ , because of the stronger inductive effect.

The electromeric effect can also exercise the opposite effect. In compounds such as nitrobenzene or benzaldehyde, the possible component structures include the following:



Hence with such groups (other examples are the  $\text{—SO}_3\text{H}$ ,  $\text{—CO}_2\text{H}$ ,  $\text{—IO}_2$  groups) the ortho- and para-positions are very strongly deactivated towards cationoid reagents, and the groups are meta-directing. On the other hand, the ortho- and para-positions are strongly activated towards anionoid reagents, and hence we find that nitrobenzene reacts with  $\text{NaOH}$  to give *o*-nitrophenol (p. 200).

The reality of the electromeric effect is shown by measurements of electric moments (*Sutton*, Proc. Roy. Soc. A 133, 668; Trans. Faraday Soc. 1934, 30, 789). In an alkyl chloride the inductive effect makes the chlorine atom more negative than the carbon to which it is attached, while in chlorobenzene there is the same effect, but in addition the electromeric effect works in the opposite direction; hence the alkyl chloride should have a larger electric moment than the aryl chloride. With the nitro-group (meta-directing) there again should be a difference between the aliphatic and aromatic compounds but in the opposite direction, because the electromeric effect makes the nitro-group in nitrobenzene more negative; hence the aromatic compound should have a larger moment than the aliphatic. The differences observed are in the expected directions: examples are:

|                                   |                           |
|-----------------------------------|---------------------------|
| $\text{Me}_3\text{CCl}$           | $\mu = 2.14$ Debye units  |
| $\text{C}_6\text{H}_5\text{Cl}$   | $\mu = 1.56$ Debye units  |
| $\text{Me}_3\text{CHNO}_2$        | $\mu = 3.29$ Debye units  |
| $\text{C}_6\text{H}_5\text{NO}_2$ | $\mu = 3.93$ Debye units. |

This discussion shows that no simple rule of orientation can be formulated. The best that can be done is to summarise as follows: If, in the orientating group, the atom attached to the ring contains unshared electrons, the electromeric effect will overcome any inductive effect, and there will be ortho-para-substitution; if an atom with unshared electrons is linked by a double bond to the atom attached to the ring there will also be a powerful electromeric effect

and substitution will take place in the meta-position; in all other cases, the inductive effect will control the result, with electron-attracting groups giving meta-substitution, and electron-repelling groups ortho-para-substitution.

In aromatic structures more complicated than benzene, *e.g.*, naphthalene, what has been said still holds true, but such compounds are not completely symmetrical: all the hydrogen atoms in naphthalene itself are not identical in position. Hence yet a third effect must come into play, the polarisation of the molecule by the field of the molecule of the substituting agent. This is probably the main reason for the preferential substitution of naphthalene in the  $\alpha$ -position with certain reagents, but the subject has not been thoroughly explored.

### Formation of the Benzene Nucleus

The reactions of aliphatic substances by means of which the benzene nucleus is synthesised are of importance chiefly because they link up the aliphatic and the aromatic compounds.

1. Methane,  $\text{CH}_4$ , when passed through a red-hot tube, gives *benzene*, among other products.

2a. Acetylene,  $\text{CH}\equiv\text{CH}$ , polymerises at a red-heat, three molecules uniting to form benzene; in the presence of  $\text{CH}_4$  and  $\text{H}_2$ , *homologues of benzene* are formed (*Meyer, Ber. 51, 1576*).

2b. Allylene,  $\text{CH}_2=\text{CH}$ , when treated with conc.  $\text{H}_2\text{SO}_4$ , polymerises to *mesitylene*, 1,3,5-trimethylbenzene.

2c. Crotonylene,  $\text{CH}_3\text{C}=\text{CH}$ , polymerises to *hexamethylbenzene*.

2d. Monobromoacetylene,  $\text{CH}\equiv\text{CBr}$ , polymerises to 1,3,5-tribromobenzene.

2e. Propiolic acid,  $\text{CH}\equiv\text{C}\cdot\text{CO}_2\text{H}$ , polymerises in sunlight to 1,3,5-benzene-tricarboxylic acid, *trimesic acid*.

2f. Acetylene-dicarboxylic dimethyl ester,  $\text{CH}_3\text{OOC}\cdot\text{C}\equiv\text{C}\cdot\text{COOCH}_3$ , polymerises in the presence of acetic acid and pyridine to give *mallonic hexamethyl ester*.

3. Carbon tetrachloride,  $\text{CCl}_4$ , and tetrachloroethylene,  $\text{CCl}_2=\text{CCl}_2$ , give *hexachlorobenzene* when passed through a hot tube. See also *hexabromobenzene* (p. 51).

4. Hexyl iodide,  $\text{C}_6\text{H}_{13}\text{I}$ , with  $\text{ICl}$  gives *hexachlorobenzene*, and with bromine *hexabromobenzene*.

5a. Geranial or citral,  $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{C}(\text{CH}_3):\text{CH}\cdot\text{CHO}$ , gives 1-methyl-4-isopropylbenzene, or *cymene*, when treated with  $\text{KHSO}_4$ .

5b. The condensation product of methyl-ethyl-acrolein and acetone,  $\text{CH}_3\cdot\text{CH}_2\text{CH}:\text{C}(\text{CH}_3)\text{CH}:\text{CH}\cdot\text{COCH}_3$ , gives *pseudocumene*.

5c. The condensation product of 2 mols. of isovaleraldehyde and 1 mol. acetone,  $(\text{C}_4\text{H}_7)\cdot\text{CH}_2\text{CH}:\text{C}(\text{C}_4\text{H}_7)\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_3$ , gives *di-isopropyl-toluene*.

6a. Acetone and conc.  $\text{H}_2\text{SO}_4$  gives *mesitylene*, 1,3,5-trimethylbenzene. Similarly methyl-ethyl-ketone gives 1,3,5-triethylbenzene, and methyl-n-propyl-ketone gives 1,3,5-tri-n-propylbenzene.

6b. Butylidene-acetone,  $\text{C}_4\text{H}_7\text{CH}:\text{CHCOCH}_3$ , gives *toluene* and a *phenol* of the cresol type when passed over  $\text{CuO}$  at  $700^\circ$ .

7. Carbon monoxide combines with potassium on heating to give the K salt of *hexahydroxybenzene*.

8. Butyryl chloride,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COCl}$  (3 mols.), condenses by means of  $\text{AlCl}_3$  to *triethyl-phloroglucinol*.

9. Nitromalonic aldehyde,  $\text{NO}_2\cdot\text{CH}(\text{CHO})_2$ , gives a Na salt which decomposes to 1,3,5-trinitrobenzene.

10. The same aldehyde condenses with acetone to give *p-nitrophenol*.

11. Hydroxymethylene-acetone (formyl-acetone),  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} : \text{CHOH}$  (3 mols.), condenses readily to 1,3,5-triacetyl-benzene,  $\text{C}_6\text{H}_3(\text{COCH}_3)_3$ ; similarly hydroxymethylene-acetophenone,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH} : \text{CHOH}$  (3 mols.), gives 1,3,5-tribenzoyl-benzene.

12. Diacetyl,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}_3$ , in presence of alkali condenses to 2,5-dimethyl-benzoquinone. Similarly the diketone  $\text{CH}_3 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_3$  gives duroquinone.

13. Hydroxymethylene-acetic ester (formylacetic ester) and its dimeric condensation product, cumalinic ester, condenses easily to the ester of trimesic acid (1,3,5-benzene tricarboxylic acid). This is also obtained by the action of Zn on a mixture of formic and chloroacetic esters.

14. Pyruvic acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CO}_2\text{H}$  (3 mols.), condenses when heated with NaOH with elimination of oxalic acid and  $\text{H}_2\text{O}$  to give methyl-dihydrotrimesic acid<sup>3</sup> the latter can be converted by loss of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  into witic acid.

15.  $\beta$ -Formylpropionic acid,  $\text{OHC} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  (2 mols.), gives terephthalic acid.

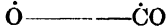
16. Acetoacetic ester,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$  (4 mols.), condenses to 3,5-dimethyl-4-carboxyphenyl- $\beta$ -methylglutaconic acid,  $(\text{C}_6\text{H}_2\text{Me}_2\text{CO}_2\text{H})\text{C}(\text{CO}_2\text{H}) : \text{C} \cdot \text{Me} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

17. The sodium derivative of acetoacetic ester reacts with  $\text{CHCl}_3$  to give hydroxy-witic ester (hydroxymethyl-isophthalic ester), which is also formed directly from methenyl-bis-acetoacetic ester with NaOEt.

18.  $\alpha, \beta$ -Dibromoglutaric ester,  $\text{CO}_2\text{R} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{R}$ , gives pyromellitic acid, 1,2,4,5-benzene-tetracarboxylic acid, on treatment with excess KOH.

19. Glutaconic ester,  $\text{CH}(\text{CO}_2\text{Et}) \cdot \text{CH} \cdot \text{CH}_2\text{CO}_2\text{Et}$  (2 mols.), condenses in presence of NaOEt with loss of EtOH and  $\text{CH}_3\text{CO}_2\text{Et}$  to give 4-hydroxy-isophthalic ester.

20. Dehydracetic acid,  $\text{CH}_3 \cdot \text{C} : \text{CH} \cdot \text{CO} \cdot \text{CH} \cdot \text{COCH}_3$ , gives orcinol, 3,5-dihydroxytoluene.



21. Acetylpyruvic ester,  $\text{MeCO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$  (2 mols.), condenses to hydroxy-toluic ester.

22. The ester  $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{C}(\text{CH}_3) \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et})_2$ , from methyl-ethyl-acrolein and malonic ester gives with NaOEt hydroxy-mesitylenic acid.

23. Citrylidene-malonic ester (Vol. II, p. 145) gives 3-isoameryl-4-methyl-salicylic acid.

The formation of mellitic acid (benzene hexacarboxylic acid) by the oxidation of graphite is not a synthesis of the benzene ring, because graphite is an aromatic substance. It consists of carbon atoms arranged in planes which lie upon one another; in each plane the carbon atoms are united to form a system of condensed benzene rings (Bernal, Proc. Roy. Soc. A 106, 749; Mauguin, Bull. soc. franç. Min. 49, 32 (1926); Finch and Wilman, Proc. Roy. Soc. A 155, 345; Hofmann and Frenzel, Ber. 63, 1248).

Summarising the reactions by which aliphatic compounds are converted into benzene derivatives by nuclear synthesis we find:

1. Some saturated compounds, such as methane (1) and carbon tetrachloride (3) form the benzene ring when heated (pyro-condensation). Many benzene derivatives, such as benzene itself, the methyl-benzenes, the simple amino- and hydroxy-benzenes, are remarkably stable at high temperatures (see coal-tar, p. 34).

2. In the perchlorination of some aliphatic compounds the formation of hexachloro-benzene has been observed. Hexyl iodide (4) gives hexachloro- and hexabromo-benzene with particular ease.

3. A great number of aliphatic acetylenic compounds containing a triple bond undergo polymerisation, three molecules uniting to form a benzene derivative. The polymerisation of acetylene to benzene (2a) is the most difficult of all; that of bromo-acetylene (2d) is much easier. Allylene (2b) and crotonylene (2c) require sulphuric acid, and

propionic acid (2e) sunlight for this polymerisation. The other aliphatic compounds which condense to form aromatic substances contain carbon doubly linked to oxygen; many are ketones, or they contain the hydroxymethylene group.

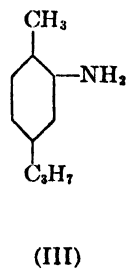
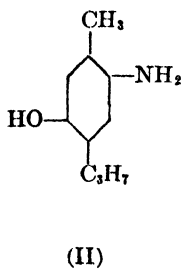
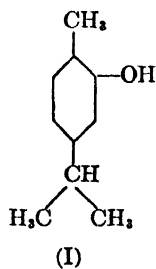
4. Direct addition reactions are exemplified by the formation of potassium hexahydroxy-benzene from CO and K (7). Examples of condensation with elimination of water are: the simple ring closure in the conversion of citral or geranial and other ketonic-olefins into cymene, pseudocumene, and di-isopropyl-toluene (5a, b, c); the condensations of acetone, methyl-ethyl- and methyl-*n*-propyl ketone into 1,3,5-trialkyl-benzenes (6a, b). The condensation of 2 mols. of  $\beta$ -forinyl-propionic acid into terephthalic acid (15) takes place with loss of both water and hydrogen. These condensations are related to the condensations of dehydracetic acid to orcinol (20), of nitro-malonic aldehyde and hydroxymethylene compounds (9, 10, 11, 13), of  $\alpha$ -diketones to quinones (12a, b), of acetylpyruvic acid into hydroxy-toluic acid (21) and of chloroform and sodio-acetoacetic ester into hydroxy-uvitic ester, in which the formation of methenyl-*bis*-acetic ester can be assumed as an intermediate product (17). The formation of homologues of salicylic acid from alkylidene-malonic esters in the presence of NaOEt takes place by means of an intramolecular acetoacetic ester condensation. The condensation of pyruvic acid to methyl-dihydro-trimesic acid, or uvitic acid (14), in which oxalic acid is eliminated, is unique.

The following are examples of the conversion of cyclohexane derivatives into benzene derivatives:

*Willstätter's synthesis* of benzene (p. 16).

Catalytic dehydrogenation. A summary of methods and results will be found in an article by *Linstead*, Ann. Rep. Chem. Soc. 33, 294 (1937). The usual reagents are sulphur, selenium, and metals, such as platinum.

Carvone (Vol. II, p. 237) isomerises on heating with KOH, phosphoric acid, or other reagents, to carvacrol (I). The latter is also formed when camphor is heated with iodine or fused with zinc chloride (Vol. II, p. 283). Carvone oxime is converted by sulphuric acid into *p*-amino-thymol (II) (*Wallach*), while thujone oxime can be converted into amino-cymene (III). Both camphor and fenchone (Vol. II, p. 315) give 1-acetyl-3,4-*o*-xylene when heated with sulphuric acid; with P<sub>2</sub>O<sub>5</sub> the former yields *p*-cymene, and the latter *m*-cymene:



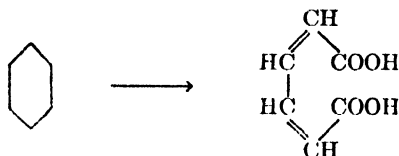
### Rupture of the Benzene Ring

As already mentioned, the stability of the benzene ring is one of its characteristic properties. It often breaks down when treated with reagents which convert it into cyclohexane derivatives, though the latter in many cases cannot be isolated. Sometimes the products still contain six carbon atoms in a chain, but usually this is not so; in some cases pentacarbo-cyclic compounds are formed from intermediate products of the type of hexacarbo-cyclic-diketones.

Ring fission is most easily brought about in phenols, aminophenols, quinones, hydroxyquinones, and phenol carboxylic acids.

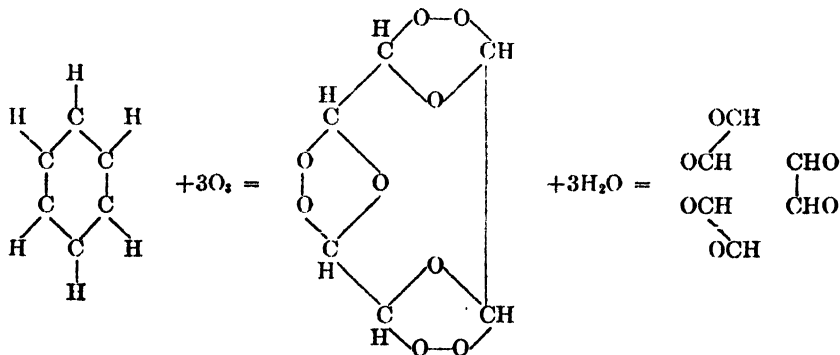
#### 1. Fission by Mild Oxidation

The mildest oxidation of benzene takes place biologically in animals. Only one double bond is ruptured and muconic acid is formed (*Jaffe*, *Z. physiol. Chem.* 62, 58):



Muconic acid is also obtained by the oxidation of *o*-benzoquinone (*Bösesken*).

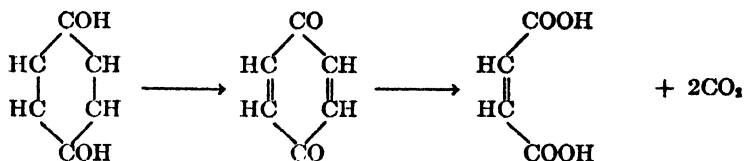
Strong oxidising agents convert benzene into carbon dioxide, formic, and oxalic acids, but ozone breaks it down smoothly in an interesting way. By addition of three molecules of ozone, benzene triozonide,  $C_6H_6O_9$ , is formed. This is decomposed by water into three molecules of glyoxal, (*Harries*; the formulation is that of *Rieche*, *Alkylperoxyde und Ozonide*, Dresden, 1931). Homologous benzene hydrocarbons behave similarly.



Catechol, 1,2-dihydroxy-benzene, and protocatechuic acid, 3,4-dihydroxybenzoic acid, are oxidised to dihydroxy-tartaric acid by nitrous acid (*Kekulé*). Catechol is decomposed by electrochemical oxidation into succinic and butyric acids; the direct oxidation prod-

uct is fumaric acid, which can be isolated if a cell with a diaphragm is used (*Fichter*, *Helv.* 2, 583).

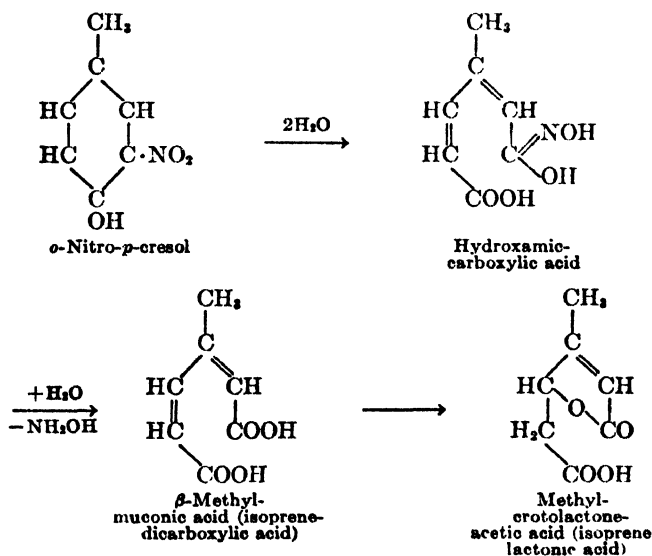
Hydroquinone, 1,4-dihydroxybenzene, and quinone, which is easily formed from it, are decomposed by silver peroxide into maleic acid and  $\text{CO}_2$  (*Kempf*):



When benzene vapour is passed, together with gases containing oxygen, over  $\text{V}_2\text{O}_5$  or other metallic oxides, at a temperature of  $400\text{--}500^\circ$ , maleic acid is formed (*Downs*, *Chem. and Ind.* 45, 188). This reaction is used industrially for the preparation of maleic acid (U. S. 1,895,522).

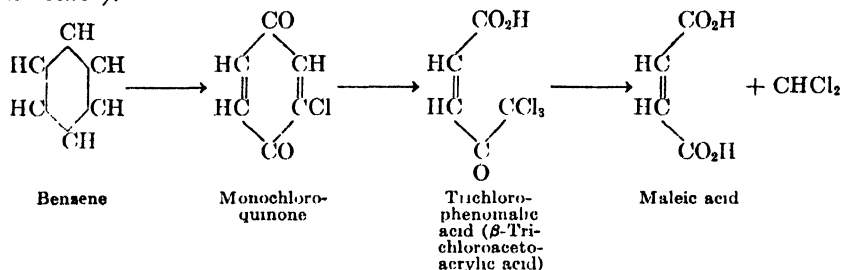
Phenol,  $\text{C}_6\text{H}_5\text{OH}$ , has been converted by  $\text{KMnO}_4$  into mesotartaric acid (*Döbner*). Quinone is probably the primary product, and this is converted into maleic acid, which gives mesotartaric acid when acted upon by  $\text{KMnO}_4$  (Vol. I, p. 658). Tert.-butyl-phenol,  $(\text{CH}_3)_3\text{C}\cdot\text{C}_6\text{H}_4\text{OH}$ , and tert.-amyl-phenol,  $(\text{C}_2\text{H}_5)(\text{CH}_3)_2\text{C}\cdot\text{C}_6\text{H}_4\text{OH}$ , give trimethyl- and ethyl-dimethyl-pyruvic acids, respectively (*Anschütz and Rauff*).

A reaction discovered by *G. Schultz* and correctly interpreted by *Pauly* (*Ann.* 416, 1) is an example of the ring being opened without degradation. When conc.  $\text{H}_2\text{SO}_4$  acts on *o*-nitro-*p*-cresol, water is taken up and  $\beta$ -methyl-muconic (isoprene-dicarboxylic) acid is formed. This goes over into  $\Delta^{\alpha\beta}$ - $\beta$ -methyl-crotolactone-acetic acid (isoprene-lactonic acid).



## 2. Fission by Simultaneous Chlorination and Oxidation

When treated with  $\text{KClO}_3$  and  $\text{H}_2\text{SO}_4$ , benzene gives first chlorinated quinones and then trichloro-phenomalic acid ( $\beta$ -trichloroacetoacrylic acid) (Vol. I, p. 481), which, when treated with aqueous baryta, decomposes into chloroform and maleic acid (*Kekulé, Strecker*).



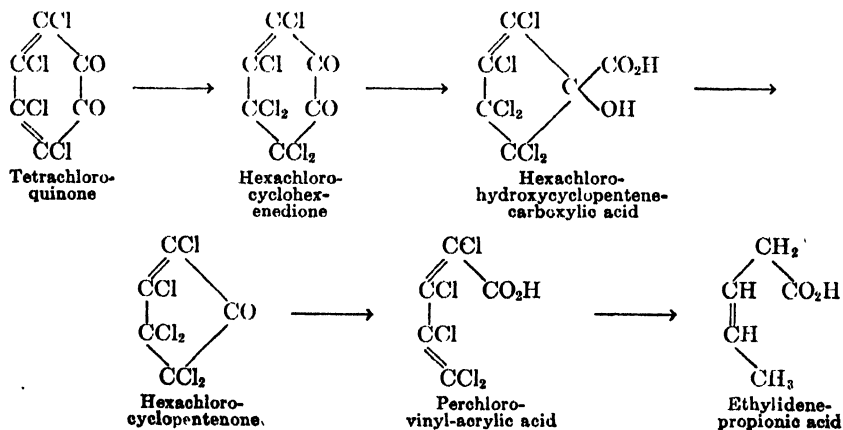
With the same reagents, phenol, salicylic (*o*-hydroxybenzoic acid), and gallic acid,  $\text{CO}_2\text{H}$  [1]  $\text{C}_6\text{H}_2$  [3,4,5] (OH)<sub>3</sub>, give trichloropyruvic (isotrichloro-glycerolic) acid,  $\text{CCl}_3\text{C}(\text{OH})_2\text{CO}_2\text{H}$  (Vol. I, p. 464).

Picric acid (2,4,6-trinitrophenol-1) gives chloropicrin (Vol. I, p. 485) when treated with bleaching powder, and bromopicrin with  $\text{Br}_2$  and lime.

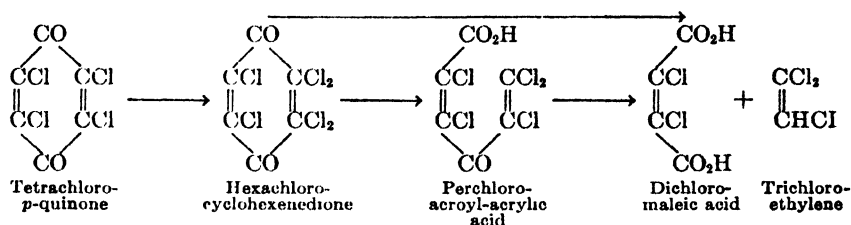
A number of interesting ring-fission reactions were investigated by *Zincke*. They involve the conversion of a suitable aromatic substance into a chlorinated cyclohexene- and cyclopentene-ketone, and the fission of the latter.

Four examples will be given, three referring to the three dihydroxybenzenes, and the fourth to phloroglucinol, 1,3,5-trihydroxybenzene.

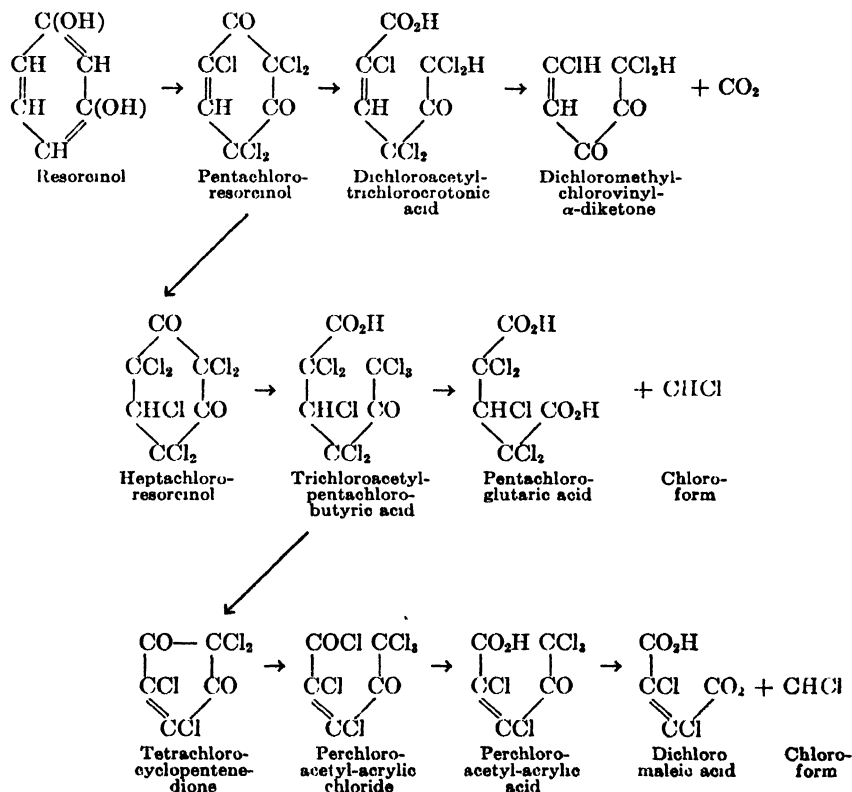
1. Catechol, *o*-dihydroxybenzene, when treated with chlorine first gives tetrachloroquinone, and then hexachloro-cyclohexenedione. The latter isomerises on heating with water to hexachloro-hydroxycyclopentenecarboxylic acid, which can be oxidized by chromic acid to hexachloro-cyclopentenone. With caustic soda this compound breaks down to perchloro-vinyl-acrylic acid, which, on reduction, gives ethylidene-propionic acid (*Zincke, Ber.* 27, 3364).



2. The decomposition of hydroquinone is simpler. Tetrachloro-*p*-quinone, chloranil, is readily obtained by the action either of chlorine on hydroquinone or quinone, or of HCl and KClO<sub>3</sub> on phenol. It takes up more chlorine to form hexachloro-cyclohexenedione, which, with alcoholic potash, is decomposed to perchloro-acroyl-acrylic acid. The latter, as well as hexachloro-cyclohexenedione itself, is decomposed by aqueous caustic soda to dichloromaleic acid and trichloroethylene (Zincke, Ann. 267, 1).



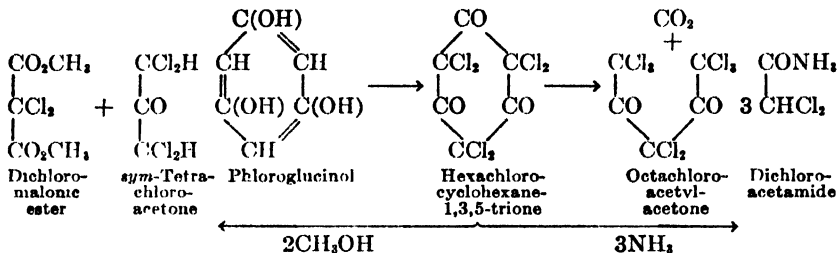
3. Resorcinol in acetic acid solution gives, with chlorine, pentachlororesorcinol and, further, heptachlororesorcinol. These two *m*-diketo-chlorides are decomposed on treatment with cold water, the penta-compound giving dichloroacetyl-trichlorocrotonic acid, and the hepta-compound with more water and chlorine forming trichloroacetyl-pentachloro-butyric acid. The former, on boiling with water, gives dichloromethyl-chlorovinyl- $\alpha$ -diketone, while the latter with





alkalis undergoes a decomposition similar to that of trichloroacetyl-acrylic acid, chloroform, and pentachloro-glutaric acid being formed. With boiling water, however, it goes over into tetrachloro-cyclopentendione, and this, with chlorine, gives perchloro-acetyl-acrylic chloride. With water, the latter is converted into the free acid, which, finally, under the action of alkalis breaks down into chloroform and dichloromaleic acid.

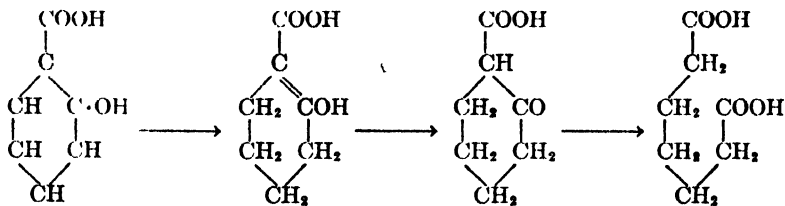
4. Phloroglucinol (1,3,5-trihydroxy-benzene) behaves quite similarly to resorcinol. With chlorine it gives hexachloro-cyclohexane-1,3,5-trione. This triketone decomposes when treated with chlorine and water into octachloro-acetyl-acetone with methyl alcohol it decomposes into dichloro-malonic dimethyl ester and *sym*-tetrachloro-acetone; with ammonia it gives three molecules of dichloroacetamide (Zincke, Ber. 23, 1706):



In these four examples, the ring opens between a CO-group and a CCl<sub>2</sub>-group of a keto-chloride. Zincke originally investigated this reaction in the naphthalene series, where it enabled him to break up one of the naphthalene rings and to convert naphthalene derivatives into indene derivatives. Later he applied the reactions to the phenols, mentioned above, and to other aromatic compounds. By similar methods Hantzsch succeeded in decomposing phenol with chlorine in alkaline solution, and in converting it into cyclopentene derivatives (Vol. II, p. 59) (Ber. 22, 1238).

### 3. Fission by Reduction in Alkaline Solution

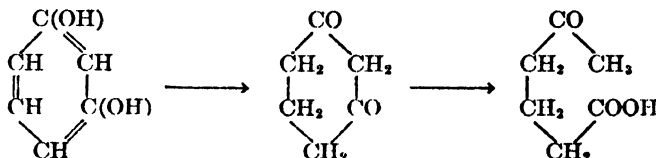
I. When phenol *o*-carboxylic acids, dissolved in amyl alcohol, are reduced with Na, the ring is opened; tetrahydro-acids and their rearrangement products, hydro-aromatic *o*-keto-carboxylic acids, probably being formed as intermediates. The latter take up water and are converted into pimelic acids. Salicylic acid gives an almost theoretical yield of *n*-pimelic acid, and *o*-, *m*-, and *p*-cresotinic acids give the three isomeric methyl-pimelic acids (Einhorn, Willstätter, Ber. 28, R 744):



The reaction has been successfully applied to the naphthalene-*o*-hydroxycarboxylic acids (p. 609).

II. Resorcinol on reduction gives dihydro-resorcinol, which is oxidised by KMnO<sub>4</sub> to *n*-glutaric acid (Merling, Ann. 278, 32).

When heated for several hours with conc. baryta water at 150–160°, dihydro-resorcinol takes up water and decomposes into  $\gamma$ -acetylbutyric acid (Vol. II, p. 112) (*Vorländer*, Ber. 28, 2348). This reaction can be reversed (Vol. II, p. 111):



## 1. THE MONONUCLEAR BENZENE HYDROCARBONS

**Benzene**,  $\text{C}_6\text{H}_6$ , m.p. +5.6°, b.p. 80.2° (760 mm.), is the parent hydrocarbon of the aromatic compounds. It is produced in the dry distillation of coal, and is therefore found in coal-tar, together with many other compounds including thiophen,  $\text{C}_4\text{H}_4\text{S}$ , a compound closely resembling it in physical properties. It is also formed, together with homologues, by the pyrolysis, with or without the application of pressure, of many open-chain compounds of high molecular weight, *e.g.*, oleic acid (cracking). Pure benzene is formed by heating benzoic acid or benzene polycarboxylic acids with soda-lime. Synthetically, benzene may be produced from acetylene by heating to high temperatures.

Benzene is obtained from coal-tar by fractional distillation and is separated from thiophene (easily detected by the indophenine or the phenanthraquinone reaction) by repeated shaking with a little conc.  $\text{H}_2\text{SO}_4$ , treatment with  $\text{AlCl}_3$ , or heating with  $\text{S}_2\text{Cl}_2$ , formaldehyde, or phthalic anhydride (*Haller*, Bull. [3], 15, 390, 1065; *Lippmann*, Mo. 23, 669; Ger. Pat. 211,239). Finally it is purified after partial crystallisation in a freezing mixture, by the removal of the residual liquid.

*History* (*cf.* *Hofmann*, Ber. 23, 1271).—Faraday discovered benzene in 1825 in compressed illuminating gas prepared from oil. *Mitscherlich*, in 1834, obtained it by distilling benzoic acid with lime. *A. W. Hofmann*, in 1845, found it in coal-tar, and *Berthelot*, in 1866, synthesised it by polymerisation of acetylene.

*Properties*.—Benzene is a mobile liquid with an ethereal odour,  $d_4^{20}$  0.8999,  $n_D^{20}$  1.50043, dielectric constant 2.272, dipole moment 0, specific exaltation of refractive index,  $E\sigma_D$  –0.22°. For the infra-red and ultra-violet absorption spectra see *Bawles*, Phys. Rev. 36, 296; for the Raman spectrum see *Grassmann*, Z. Physik, 86, 321; for a detailed investigation of the various spectra see *Ingold* and co-workers, J. 1936, 912 *et seq.* It burns with a luminous, very sooty flame. It is miscible with dry alcohol and ether, and dissolves resins and fats readily. It also dissolves many hydrocarbons, some of which separate in the form of crystals containing benzene of crystallisation (*e.g.*, triphenylmethane). Sulphur, iodine, and phosphorus are also soluble in benzene. The vapour, when inhaled, exerts an intoxicating and stupefying effect.

*Reactions*.—1. When passed through a hot tube benzene is partly converted into diphenyl,  $\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_5$ , and diphenyl-benzenes, such as  $\text{C}_6\text{H}_5(\text{C}_6\text{H}_5)_2$ . It also decomposes to some extent into acetylene.

2. When benzene is oxidised with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$ , owing to the intermediate formation of diphenyl and polyphenyls, some benzoic acid and a little *o*-phthalic acid are formed, but benzene is very stable to most oxidising agents. Silver peroxide in presence of nitric acid oxidises it to quinone, and manganic sulphate does the same (*Kempf*, Ber. 38, 3963). With  $\text{KClO}_3$  and  $\text{H}_2\text{SO}_4$  the ring opens and trichloro-phenomalic acid ( $\beta$ -trichloroaceto-acrylic acid) is formed (p. 30). When ozone is passed through benzene for some time, a white, amorphous, and explosive triozone is obtained; this is slowly decomposed by water to glyoxal (*Haries*, Ber. 37, 3431; p. 28).

3. When heated with  $\text{H}_2$  at  $260\text{--}280^\circ$ , benzene is largely reduced with isomerisation to methyl-cyclopentane (Vol. II, p. 47). It can be reduced to cyclohexane by passing its vapour with hydrogen over finely divided Ni at  $180\text{--}200^\circ$  (*Sabatier*, *Senderens*, C. r. 132, 566), or at lower temperatures by using the platinum metals (*Willstätter*, *Skita*).

4. Chlorine and bromine act both by addition and substitution; an anti-catalytic effect of oxygen has been found by *Luther* and *Goldberg* (*Z. physikal. Chem.* 56, 43). For the action of  $\text{HOCl}$  and  $\text{Cl}_2\text{O}$ , see *Homer*, J. 100, 276.

5.  $\text{HNO}_3$  transforms benzene into nitrobenzene,  $\text{C}_6\text{H}_5\text{NO}_2$ .

6.  $\text{H}_2\text{SO}_4$  converts it into benzene-sulphonic acid,  $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ .

7. By means of  $\text{AlCl}_3$  and alkyl halides, alkyl residues may be introduced into benzene (4th method of formation of benzene hydrocarbons, p. 38) (*Kranzlein*, *Aluminiumchlorid*, Berlin, Verlag Chemie, 1933). On continued heating with  $\text{AlCl}_3$ , naphthalene is formed, diethylbenzene being an intermediate (*Homer*, loc. cit).

8. Benzene condenses with aldehydes in presence of  $\text{H}_2\text{SO}_4$  to aromatic hydrocarbons, e.g., diphenylmethane and -ethane.

9. Electrochemical oxidation converts it into phenol, catechol, hydroquinone, quinone, and finally maleic acid (*Fichter*, Ber. 47, 2003). The last-named compound is also obtained by passing benzene vapour over  $\text{V}_2\text{O}_5$  at  $400\text{--}450^\circ$ . When benzene burns slowly at temperatures between  $380^\circ$  and  $565^\circ$ , phenol and benzoquinone are formed (*Amiel*, *Ann. chim.* [XI], 7, 70).

### Coal-Tar

Dry distillation of coal gives rise to benzene together with many alkyl benzenes and more highly condensed aromatic compounds, such as naphthalene,  $\text{C}_{10}\text{H}_8$ , acenaphthene,  $\text{C}_{12}\text{H}_{10}$ , fluorene,  $\text{C}_{13}\text{H}_{10}$ , anthracene and phenanthrene,  $\text{C}_{14}\text{H}_{10}$ , fluoranthene,  $\text{C}_{15}\text{H}_{10}$ , pyrene,  $\text{C}_{15}\text{H}_{10}$ , chrysene,  $\text{C}_{18}\text{H}_{12}$ , also phenols, and heterocyclic compounds, such as thiophene, pyridine, quinoline, acridine, etc. They are found in the "coal-tar," obtained in large quantities in gas-works and coke-ovens. About one-fifth of the total produced is gas tar, and four-fifths coke tar. In addition to illuminating gas and tar, ammoniacal liquor is formed, while coke, a fuel richer than coal itself in carbon, is left in the retorts.

The rapid and brilliant development of aromatic organic chemistry was largely due to the fact that the fundamental aromatic compounds have been available for chemical investigation in any desired quantity. Whereas the paraffins are unsuitable starting materials for the synthesis of aliphatic substances, the aromatic hydrocarbons, with their power to enter into the most varied reactions, form not only the theoretical, but also the practical basis for the synthesis of aromatic compounds. Coal-tar, which contains these hydrocarbons, is the inexhaustible source for preparing innumerable aromatic compounds, many of which have had most useful applications as dyes, perfumes, and drugs.

*The treatment of coal-tar for aromatic hydrocarbons.*—When coal is distilled at a comparatively low temperature, not greatly exceeding 600° (Vol. I, p. 100), the so-called "low-temperature" tar is obtained. This contains, in addition to phenols, various hydrocarbons which are not benzene homologues, but paraffins, olefins, so-called naphthenes (Vol. II, p. 64), and partially hydrogenated aromatic hydrocarbons. There is no naphthalene. Benzene derivatives are exclusively obtained from high-temperature tar, which is produced at 1100–1300° in gas retorts, and at 900–1100° in coke ovens. The difference in the temperature used is shown in the different composition of the two tars; gas tar, owing to the higher temperature of its formation, is richer in high-boiling substances and pitch.

Crude tar contains about 2–5% of water, derived partly from the moisture present in the coal, and partly produced by the coking process, and about 1% of ammonia and organic bases. The remainder is a mixture of pitch and tar-oils, with more or less free carbon. It is first freed from water, and then fractionated from steel retorts which may hold as much as 50 tons. Usually four fractions are taken, the separation being on the basis of their mean specific gravities but occasionally on that of the temperature of distillation:

1. Light Oil, 2–5%, sp. gr. 0.91–0.99, boiling below 160°.
2. Middle Oil, 10–12%, sp. gr. 1.01–1.02, boiling approximately between 150° and 240°.
3. Heavy Oil, 8–10%, sp. gr. 1.03–1.04, boiling approximately between 240° and 270°.
4. Green, or Anthracene Oil, 18–25%, sp. gr. 1.08–1.09, boiling approximately between 270° and 370°.

The residue, 50–60%, is pitch.

The gases escaping during distillation, as well as those from the coke ovens, are rich in benzene and its lower homologues; they also contain more than 50% of hydrogen. The hydrocarbons are absorbed in scrubbers containing oil obtained from the tar itself and are isolated by distillation. About 90% of the production of benzene is derived from these gases.

Each of the four tar fractions is distilled into sub-fractions. From these the phenols are removed by means of caustic soda and the bases by dilute sulphuric acid. From the light oil a mixture of hydrocarbons is obtained from which olefins and other unsaturated compounds are removed with concentrated sulphuric acid. The oils are then washed with water, dried, and subjected to careful fractional distillation with a column, the higher boiling fractions sometimes *in vacuo*. In this manner the light oil is separated into 50% benzene, 6–10% toluene, 2–3% xylenes, 12–15% naphthalene, 8–10% phenols, and 1–3% pyridine bases. The middle oil contains the industrially important phenols, with naphthalene, bases, and some of the constituents of the light and heavy oils. The phenols and bases are removed as described for the light oil. The subsequent fractional distillation must be carried out so as to take account of the high melting point of naphthalene, which solidifies at 80°. The same applies to heavy oil which contains naphthalene, diphenyl, acenaphthene, and

**DISTILLATE**  
(the percentages are approximate; each fraction is 10% of its neighbour)

[illegible]

\* From *Ullman, Encyclopädie der Technischen Chemie*, 1932, IX, p. 648.

other substances which crystallise easily. When these substances have been extracted, the heavy oil is used as a fuel, and also as a solvent for the absorption of benzene from the gases, as has been mentioned above. The greenish-yellow anthracene oil solidifies at ordinary temperature. Its most valuable constituent is anthracene, which is present to the extent of about 20–30%. In addition it contains the isomeric phenanthrene, carbazole, and other substances. The liquid fraction is used as a motor fuel and lubricant.

In addition to benzene, the following benzene hydrocarbons occur in coal-tar: toluene (methyl-benzene), the three isomeric xylenes (dimethyl-benzenes), ethyl-benzene, vinyl-benzene (styrene), the three isomeric trimethyl-benzenes (mesitylene, *pseudo*-cumene, hemimellitene), *n*-propyl-benzene, the three isomeric ethyl-toluenes, and durene (*sym*-tetramethyl-benzene). Aromatic hydrocarbons are also found in considerable quantity in lignite tar, to some extent in wood tar oil, in shale tar oil, and in Rumanian and Dutch East Indian petroleum. A list of coal-tar constituents is given in the table on p. 36.

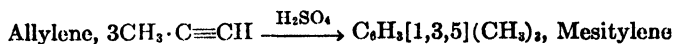
The production of aromatic substances by dry distillation should be considered in connection with their formation by *pyrogenic synthesis* or *pyro-condensation*, brought about by leading simple aliphatic bodies such as  $\text{CH}_4$ ,  $\text{EtOH}$ , and  $\text{Et}_2\text{O}$ , together with  $\text{H}_2$ , through red-hot tubes (*Haber*, Ber. 29, 2691). Acetylene and allylene are probably intermediates. Just as acetylene produces benzene, a mixture of acetylene and allylene might give toluene, benzene and acetylene might give naphthalene, etc. (*Berthelot*, Ann. 139, 281; *Jacobsen*, Ber. 10, 853; 19, 2513; *Schulze*, Ber. 18, 3032; *Ferko*, Ber. 20, 660). For the pyrolysis of butadiene hydrocarbons see *Staudinger*, Ber. 46, 2465. In the dry distillation of coal the volatile products come in contact with the heated walls of the retort, and hence conditions exist for such pyro-condensation. On the other hand, the composition of the coal itself is clearly of great importance.

The results of *Pictet's* experiments on the extraction of coal with benzene, and on the distillation of coal *in vacuo* (Ber. 44, 2486; 46, 3342) are of considerable theoretical interest. Their purpose was "to throw some light on the two industrially and scientifically significant questions of the formation of coal from plant matter and of its reactions during dry distillation." A French bog-head coal from Montrambert, Loire, extracted with benzene, gave a mixture of hydro-aromatic hydrocarbons, from which only hexahydro-fluorene,  $\text{C}_{12}\text{H}_{16}$ , could be isolated. When distilled at 10 mm. pressure and at a temperature not exceeding  $450^\circ$  it yielded, without producing gas, about 4% of a "vacuum-tar." The water, about 1.5% of the weight of the coal, had an acid reaction, and was free from ammonia; the coke was loose and more easily inflammable than ordinary coke. On pyrolysis the vacuum tar generated much gas, a considerable amount of ammoniacal liquor, and a tar smelling like ordinary coal-tar and containing phenol, bases smelling of pyridine, benzene, naphthalene and anthracene. The vacuum tar must have contained hydro-aromatic compounds. Since none of the above-mentioned compounds could be detected in the vacuum tar, the experiment confirms the view that the volatile compounds of more complex structure are pyrolytic products formed at a high temperature.

### Alkyl-Benzenes, $\text{C}_n\text{H}_{2n-6}$

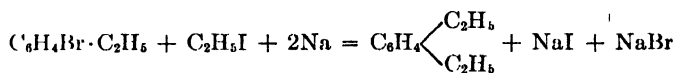
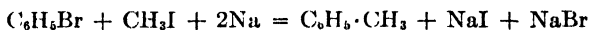
**Formation.**—A number of alkyl-benzenes occurring in coal-tar have been mentioned in the preceding section. The most important of the general methods of formation are those involving nuclear synthesis.

1. The formation of *sym*-trialkyl-benzenes from alkyl-acetylenes by polymerisation in the presence of sulphuric acid has often been mentioned. It is analogous to the formation of benzene by polymerisation of acetylene (p. 25).



Instead of alkyl-acetylenes, ketones, such as acetone and ethyl-methyl-ketone, can be treated with sulphuric acid (p. 25).

2. The reaction discovered by *Fittig* in 1864 is much more general. It consists of the action of sodium on a mixture of a brominated benzene hydrocarbon and an alkyl bromide or iodide. The reaction is carried out in ether solution (*Tollens, Fittig, Ann.* 129, 369; 131, 303; *Krafft, Ber.* 21, 3185):



This reaction is a valuable extension of the Wurtz synthesis of paraffins by the action of sodium on alkyl halides (Vol. I, p. 96). The addition of a few drops of ethyl acetate accelerates the reaction. The higher the molecular weight of the alkyl iodide, the smoother is the reaction. The first phase of the reaction is the formation of sodio-aryls and alkyls, and then free aryls are produced. Their presence can be shown by adding triphenylmethyl with which they combine to give compounds such as tetraphenylmethane (*Goldschmidt, Ber.* 59, 348; *Gilman, Am.* 55, 2893).

*Houben's* method (*Ber.* 36, 3083; *Bert., C. r.* 186, 587) is similar to *Fittig's*, the Mg halide-compounds of aryls and alkyls in ligroin or cyclohexane being used in place of the halides.

3. The syntheses of isopropyl-benzene from benzal chloride and zinc methyl and of one of the amyl-benzenes from benzal chloride and zinc ethyl (*Liebmann, Ber.* 13, 45), are analogous to that of tetramethylmethane from 2,2-dichloropropane and zinc methyl (Vol. I, p. 96).



4. A method of very general utility, which has recently been applied also to aliphatic and hydroaromatic compounds (*Unger, Ber.* 65, 467; *Hopf, ibid.* 482), is the so-called aluminium chloride synthesis discovered by *Friedel and Crafts* in 1877; it consists of the action of alkyl halides on benzene hydrocarbons in the presence of aluminium chloride.

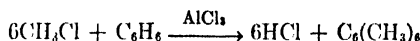
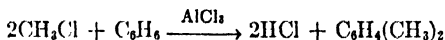
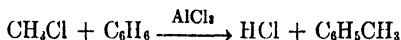
In some cases olefins in the presence of HCl react similarly to the alkyl halides (*Ger. Pat.* 184,230).

A similar reaction takes place with zinc chloride and especially with ferric chloride (*Nencki, Ber.* 32, 2414) *Wertyporoch, Ber.* 66, 1232) and also with boron tri-chloride and its addition products (*Ger. Pat.* 513,414). Aluminium chloride can sometimes be replaced by a mixture of mercuric chloride and aluminium filings (*Korczynski, Ber.* 35, 868).

The chemistry of the Friedel-Crafts reaction has been studied by *Wieland and Bettag* (*Ber.* 55, 2246), *Wohl* and *Wertyporoch* (*Ber.* 64, 1357), *Wertyporoch* and

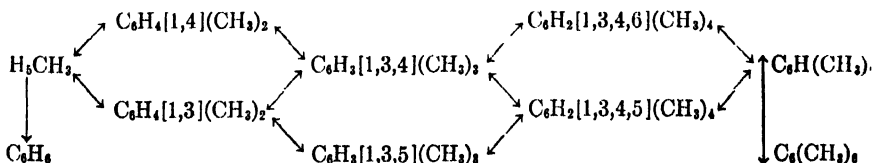
*Firla* (Ann. 500, 281). The compound first formed is presumably a ternary one, in which there is some kind of union between the aluminium chloride and the other two reactants, and the actual reaction must take place inside this complex. Intermediate compounds have often been isolated, particularly in the hydroaromatic series. In the reaction between benzene, ethyl chloride, and aluminium chloride, a compound,  $\text{Al}_2\text{Cl}_6 \cdot \text{C}_6\text{H}_5 \cdot \text{Et}$ , a yellow oil, b.p. (12 mm.)  $135\text{--}138^\circ$ , is formed (*Gustawson, Schleicher*, J. pr. 105, 355); this, in the presence of HCl, is able to convert another molecule of benzene into triethylbenzene. Thus a large quantity of benzene is alkylated by a small amount of aluminium chloride. In many other cases aluminium chloride adds on to the reaction product and has to be used in the stoichiometric amount. Sometimes hydrogenation and dehydrogenation reactions take place at the same time, e.g., the formation of *p*-propylbenzene and 1,2-diphenylpropane from benzene, allyl bromide, and aluminium chloride.

Water decomposes the compound  $2\text{AlCl}_3 \cdot \text{C}_6\text{H}_5\text{Et}$  into  $\text{Al}(\text{OH})_3$ , HCl, and triethylbenzene. All the hydrogen atoms of benzene can be replaced without difficulty (*Jacobsen*, Ber. 14, 2624; *Galle*, Ber. 16, 1745). Dilution with  $\text{CS}_2$  is sometimes an advantage (*Anschütz*, Ann. 235, 207; *Lucas*, Ber. 29, 2884):



Reactions of the same kind take place between benzene hydrocarbons and various types of halogen compounds, such as  $\text{CHCl}_3$  (cf. triphenylmethane) and the acid chlorides; see benzophenone, acetophenone, tolyl aldehyde ( $\text{CO} + \text{HCl}$  in presence of cuprous chloride react like the unknown formyl chloride,  $\text{HCOCl}$ , and  $\text{HCN} + \text{HCl}$  like  $\text{HC}(\text{Cl})\text{NH}$  (*Gattermann*, Ann. 347, 347)), resacetophenone [ $\text{MeCN}$  and  $\text{HCl}$  react like  $\text{MeC}(\text{Cl})\text{NII}$  (*Hoesch*, Ber. 50, 462)]. Diethyl ether also reacts with benzene hydrocarbons in the presence of aluminium chloride, with the formation of poly-ethyl-benzenes (*Jannasch*, Ber. 32, 2391). Aliphatic alcohols and alkyl chloroformates have also been used for preparing alkyl-benzenes by means of aluminium chloride [*Kunkell*, J. pr. 86, 518; 87, 227; *Zukerwanik*, Russ. J. 5, 764 (1936)].

*Degradation reactions.*—5. Curiously enough, aluminium chloride can be used for degrading the alkyl-benzenes as well as for synthesising them. By the action of aluminium chloride alone, or still more easily by passing HCl through a polyalkylbenzene to which aluminium chloride has been added, side-chains are split off as alkyl chlorides (*Anschütz*, Ann. 235, 177). Under suitable conditions side chains can be transferred from one hydrocarbon to another by means of aluminium chloride. Certain positions of the alkyl groups are favoured in both synthesis and decomposition, as is illustrated by the following scheme (*Anschütz*, Ber. 18, 657):



By a secondary action of aluminium chloride, the alkyl side-chains of the butyl-, amyl-, etc., benzenes often undergo rearrangement to isomeric forms. The degradation is particularly easy in the presence of much of the aromatic compound and little aluminium chloride, e.g., with poly-ethyl- and poly-isopropyl-benzenes, but not with xylenes (*Boediker*, Bull. 19, 444).

If bromine is allowed to react with a poly-alkylbenzene in the presence of



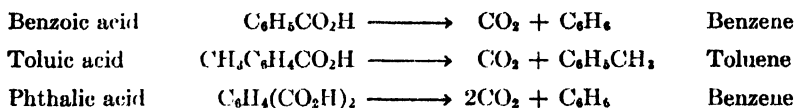
aluminium bromide, the longest of the side chains is split off and the products are brominated. (*Bodroux*, Bull. [3] 19, 888).

6. Conc.  $\text{H}_2\text{SO}_4$  has also been used for synthesis and degradation (see durene, p. 46).

7. Propyl-, isopropyl- and some other alkyl-benzenes have been prepared successfully by reducing the corresponding compounds with an unsaturated side chain, e.g.,  $\text{PhCH}:\text{CHMe}$ ,  $\text{PhCMe}:\text{CH}_2$ , with sodium in ethyl alcohol (*Klages*, Ber. 37, 1721).

Benzene itself as well as its alkyl-homologues are obtained by the following methods:

8. The dry distillation of an aromatic acid with lime or soda-lime. Iron filings are sometimes added to promote conduction of heat through the mixture. All carboxyl groups are removed and the parent hydrocarbon is formed:



9, 10, and 11. In these reactions, groups attached to the ring are replaced by hydrogen.

9. Diazo-compounds are treated with alcohol, stannous oxide in alkaline solution, or some other reducing agents (p. 122). This reaction has been particularly important for establishing the constitution of certain compounds. The diazo-compounds are obtained from amino-compounds, and these from the nitro-compounds, the reaction products of nitric acid with hydrocarbons.

10. Sulphonic acids (p. 174) are treated with superheated steam ( $180^\circ$ ) in the presence of sulphuric, conc. hydrochloric, or phosphoric acid.

11. Oxygen derivatives, such as phenols or ketones, are heated with zinc dust (*Baeyer*, Ann. 140, 295), or HI and phosphorus. It should be noted that a substance such as benzophenone,  $\text{Ph}\cdot\text{CO}\cdot\text{Ph}$ , can be reduced with ease, but diphenyl ether,  $\text{Ph}\cdot\text{O}\cdot\text{Ph}$ , not at all. Ketones are reduced smoothly when, as vapour, they are passed with hydrogen over finely divided nickel at  $190\text{--}195^\circ$  (*Darzens*, C.r. 137, 868). A very useful method for reducing aromatic ketones to hydrocarbons is *Clemmensen's* method with amalgamated zinc and alcoholic HCl (Ber. 47, 681). Another which has been used frequently is to convert the ketone into its hydrazone or semicarbazone, and heat this with solid NaOH or with NaOEt in a sealed tube (*Wolff*, Ann. 394, 86; *Kishner*).

*Properties.*—The lower benzene hydrocarbons are volatile liquids, and the higher compounds, such as the polymethyl-benzenes, durene, isodurene, penta- and hexamethyl-benzene, and hexaethylbenzene, are solid at ordinary temperature. The smell is characteristic and not unpleasant. They are insoluble in water, but are miscible with alcohol and ether, and are themselves good solvents for many organic compounds; the latter are often precipitated from these solutions by petroleum ether.

*Reactions.*—On reduction, especially when their vapours are passed with hydrogen over finely divided nickel, the alkyl-benzenes are

converted into homologues of cyclohexane, in the same way as benzene itself. At the same time considerable amounts of methane are formed (*Mailhe*, C.r. **193**, 60, 176). With HI they undergo isomeric change into cyclopentane derivatives.

2. The behaviour of the alkyl-benzenes on oxidation is of great importance. Dilute nitric acid, chromic acid,  $\text{KMnO}_4$ , and  $\text{K}_2\text{Fe}(\text{CN})_6$ , convert the side-chains into  $\text{CO}_2\text{H}$  groups. From the number of  $\text{CO}_2\text{H}$  groups formed, and from their positions, the number and relative position of the alkyl radicals in the original benzene hydrocarbon can be established. When the side chains are long, intermediate products can be obtained by careful oxidation, especially with  $\text{KMnO}_4$ , the oxidation following the same kind of course as with aliphatic compounds (*cf.* the aromatic carboxylic acids).

3. Chlorine and bromine in the dark, at ordinary temperature, and in presence of carriers, replace the hydrogen atoms of the benzene residue. At higher temperatures and in sunlight, the hydrogen atoms of the side chain are replaced.

4. Concentrated nitric acid gives nitro-compounds. If, however, the temperature is high, there is usually some oxidation of the side chain.

5. Concentrated sulphuric acid when heated with the alkyl-benzenes gives sulphonic acids; if the acid contains excess of  $\text{SO}_3$ , the reaction takes place at lower temperatures. The sulphonic acids can be reconverted into the hydrocarbons (p. 40), so that sulphonation can be used for separating and purifying benzene homologues.

6. Like benzene, the alkyl-benzenes unite with ozone to form explosive tri-ozonides, which are decomposed by water with the formation of aliphatic dialdehydes (*Harries*, Ann. **343**, 369). Oxygen hardly attacks the alkyl-benzenes at all, even at  $100^\circ$ , and when acting for several weeks; minute quantities only of mono-aldehydes and mono-carboxylic acids are formed (*Stephens*, Am. **48**, 1824). Catalytic oxidation converts ethyl-benzene into acetophenone, and isopropyl-benzene into dimethylphenyl-carbinol. Autoxidation of toluene in sunlight produces benzaldehyde and benzoic acid; the xylenes yield toluic and phthalic acids; *o*-xylene, however, does not give phthalic acid (*Ciamician*, Atti R. Accad. Lincei, **20**, 673). In addition, peroxides are formed (*Suida*, Ber. **45**, 2909).

For the action of other oxidising agents see p. 34. For the electrochemical oxidation of benzene homologues see *Fichter* and *Müller*, Helv. **18**, 831.

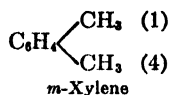
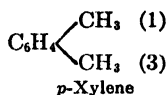
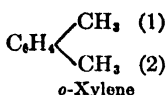
7. With chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , the homologues of benzene give compounds which, with water, give aromatic aldehydes and ketones.

8. Acetylene in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{HgO}$  or  $\text{HgSO}_4$  reacts with alkyl-benzenes giving ethylidene-aryls of the type  $\text{MeCH}(\text{C}_6\text{H}_4 \text{ alk})_2$  (*Reilly*, Am. **50**, 2564).

9. When gaseous benzene hydrocarbons are strongly heated, pyro-condensation takes place. Benzene gives diphenyl, toluene gives dibenzyl, stilbene and anthracene (*Meyer*, Mo. **37**, 681).

**Isomerism.**—Theory requires that toluene, the first homologue of benzene, should exist in one modification only and actually only one is known. The six hydrogen atoms of benzene are equivalent (p. 2).

The disubstitution product, dimethyl-benzene or xylene, is known in three isomeric forms:



Ethyl-benzene,  $\text{C}_6\text{H}_5 \cdot \text{C}_2\text{H}_5$ , is isomeric with the xylenes:

Eight isomers of the formula  $\text{C}_9\text{H}_{12}$  are possible, and all are known: (1) three trimethyl-benzenes, (2) three ethyl-methyl-benzenes, (3) two propyl-benzenes, the *n*- and the *iso*-propyl compound.

Thus, the isomeric relationships are determined by the position, number, homology, and isomerism of the alkyl groups which replace the hydrogen atoms of benzene.

**Constitution.**—The safest conclusions as to the constitution of the alkyl-benzenes are those deduced from *Fittig's* synthesis (p. 38), since intramolecular rearrangements do not take place in the course of this reaction, so far as is known, and the alkyl groups take the places formerly occupied by the halogen atoms. Oxidation is also important for determining the number and positions of the side chains (see above).

The following table shows the more important alkyl-benzenes and their properties:

| Name and Formula                                                                                   | M.p. | B.p.   | d.             |
|----------------------------------------------------------------------------------------------------|------|--------|----------------|
| <b>Toluene</b> $\text{C}_6\text{H}_5\text{CH}_3$                                                   | −95° | 110.8° | 0.8812 (20/4°) |
| <b>Xylene</b> , dimethylbenzene $\text{C}_6\text{H}_4(\text{CH}_3)_2$                              |      |        |                |
| <i>o</i> -Xylene                                                                                   | −25° | 146°   | 0.8932 (0°)    |
| <i>m</i> -Xylene, <b>isoxylene</b>                                                                 | −54° | 139°   | 0.8815 (0°)    |
| <i>p</i> -Xylene                                                                                   | +14° | 138°   | 0.8801 (0°)    |
| <b>Ethylbenzene</b> $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$                                   | −93° | 136°   | 0.8845 (0°)    |
| <b>Trimethylbenzene</b> $\text{C}_6\text{H}_3(\text{CH}_3)_3$                                      |      |        |                |
| 1,2,3-Hemimellitene                                                                                | ...  | 175°   | 0.8913 (22/4°) |
| 1,2,4-Pseudocumene                                                                                 | −61° | 170°   | 0.8805 (14°)   |
| 1,3,5-Mesitylene                                                                                   | −53° | 164.9° | 0.8634 (20°)   |
| <b>Methylethylbenzene</b> $\text{C}_6\text{H}_4(\text{CH}_3)(\text{C}_2\text{H}_5)$                |      |        |                |
| <i>o</i> - or 1,2-                                                                                 | ...  | 165°   | 0.8841 (16°)   |
| <i>m</i> - or 1,3-                                                                                 | ...  | 162°   | 0.8690 (18°)   |
| <i>p</i> - or 1,4-                                                                                 | ...  | 162°   | 0.8664 (16°)   |
| <b>-Propylbenzene</b> $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$                      | ...  | 158.5° | 0.8810 (0°)    |
| <b>Isopropylbenzene, cumene</b> $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$                     | ...  | 153°   | 0.8798 (0°)    |
| <b>Tetramethylbenzene</b> $\text{C}_6\text{H}_2(\text{CH}_3)_4$                                    |      |        |                |
| 1,2,3,4-                                                                                           | −4°  | 204°   | 0.9044 (16°)   |
| 1,2,3,5- = Isodurene                                                                               | +52° | 196°   | 0.8961 (0/4°)  |
| 1,2,4,5- = Durene                                                                                  | 80°  | 194°   | .....          |
| <b>Methylisopropylbenzene</b> $\text{C}_6\text{H}_4(\text{CH}_3)-$<br>$[\text{CH}(\text{CH}_3)_2]$ |      |        |                |
| 1,2-                                                                                               | ...  | 175°   | 0.8902 (0°)    |
| 1,3-                                                                                               | ...  | 175°   | 0.8628 (17°)   |
| 1,4- = <b>Cymene</b>                                                                               | −73° | 176°   | 0.863 (15°)    |
| <b>tert.-Butylbenzene</b> $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_3$                            | −60° | 169.3° | 0.8671 (20°)   |
| <b>Pentamethylbenzene</b> $\text{C}_6\text{H}(\text{CH}_3)_5$                                      | 53°  | 231°   | .....          |
| <b>Hexamethylbenzene</b> $\text{C}_6(\text{CH}_3)_6$                                               | 166° | 264°   | .....          |
| <b>Pentaethylbenzene</b> $\text{C}_6\text{H}(\text{C}_2\text{H}_5)_5$                              | 226° | 277°   | 0.8985 (19°)   |
| <b>Hexaethylbenzene</b> $\text{C}_6(\text{C}_2\text{H}_5)_6$                                       | 126° | 298°   | .....          |

From this table it is seen that isomeric compounds of the same formula, such as the three xylenes, have almost the same boiling

points. Among the xylenes, the *o*-compound has the highest boiling point, the *m*-compound the next lower, and the *p*-compound the lowest boiling point of the three, though it melts at the highest temperature. Durene and isodurene (tetramethyl-benzenes), pentamethyl-, hexamethyl-, and hexa-ethylbenzenes are solids at room temperature.

Introduction of a methyl group raises the boiling point of a methylbenzene by 24–30°, as can be seen from the data for toluene, the xylenes, and the more highly methylated benzenes. Introduction of a methyl group into the side chain raises the boiling point by about 24°, as can be seen from the data for toluene, ethylbenzene, and *n*-propylbenzene.

For optical and other physical constants of the benzene hydrocarbons see *Auwers*, Ann. **419**, 92.

**Toluene**,  $C_6H_5 \cdot CH_3$ . The name comes from Tolu balsam, from which it can be obtained by dry distillation. It is found in coal-tar together with thiotoluene, methylthiophene (Vol. IV), and, like benzene, is of importance industrially. It is formed by the general methods:

1. From bromobenzene by the action of methyl iodide and sodium.
2. From benzene by the action of methyl chloride and aluminium chloride.
3. By the action of aluminium chloride on polymethylbenzenes
4. From the three toluic acids, and the methylbenzene-polycarboxylic acids, on distillation with lime.

On reduction, toluene is converted into methylcyclohexane, on oxidation with dilute nitric acid or chromic acid into benzoic acid, and with chromyl chloride,  $CrO_2Cl_2$  and water, or manganese dioxide and sulphuric acid, or ceric sulphate, into benzaldehyde. On nitration it gives *o*- and *p*-nitrotoluenes, and on sulphonation much *p*- and a little *o*-toluene sulphonic acid. Its electric moment is 0.4 D.

The action of chlorine on toluene is noteworthy. At the boiling point and in sunlight, only the hydrogen atoms of the side-chain are replaced to give

benzyl chloride,  $C_6H_5CH_2Cl$ ,  
benzal chloride,  $C_6H_5CHCl_2$ , and  
benzotrichloride,  $C_6H_5CCl_3$ .

In the cold, on the other hand, *o*- and *p*-chlorotoluenes,  $C_6H_4Cl \cdot Me$ , are formed. In presence of iodine or ferric chloride, chlorine enters the ring only, even at the boiling point. (*Beilstein*, Ann. **139**, 311). On the other hand, a small quantity of  $PCl_5$  is said to facilitate the entrance of chlorine into the side-chain (*Erdmann*, Ann. **272**, 150).

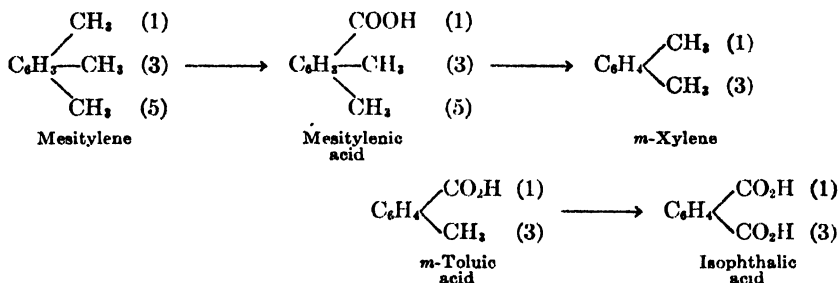
**THE HYDROCARBONS**,  $C_8H_{10}$ . There are three xylenes, or dimethylbenzenes, and one ethylbenzene. The three xylenes are found in coal-tar, *m*- (or *iso*-) xylene being most abundant, and the most important of the three from the industrial point of view.

*o*- and *p*-Xylenes are oxidised by dilute nitric acid first to *o*- and *p*-toluic acids, and then to *o*- and *p*-phthalic acids; *m*-xylene is attacked with greater difficulty. Potassium permanganate similarly oxidises the three xylenes to the corresponding toluic and phthalic acids. Ordinary sulphuric acid dissolves *o*- and *m*-xylenes;

xylene sulphonic acids are formed and can be separated by means of their salts or sulphonamides (*Jacobsen*, Ber. 10, 1013; 14, 2625). When crude xylene is steam-distilled, *p*-xylene passes over first. For the separation of the three xylenes see *Williams*, J. 1930, 37.

***o*-Xylene.** *o*-Xylene can be obtained by the action of methyl iodide and sodium on *o*-bromotoluene;  $\text{KMnO}_4$  converts it into phthalic acid, but chromic acid oxidises it completely to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , as is the case with many *o*-derivatives. Its electric moment is 0.5, D.

***m*-Xylene.** The formation of *m*-xylene from mesitylenic acid by heating with lime was of theoretical importance, because the reaction links *m*-xylene to mesitylene, in which the three methyl groups were known to be in the 1,3,5-positions. It follows that the toluic and phthalic acids which are obtained in the oxidation of *m*-xylene are meta-compounds (p. 13). The electric moment of this compound is 0.4 D.



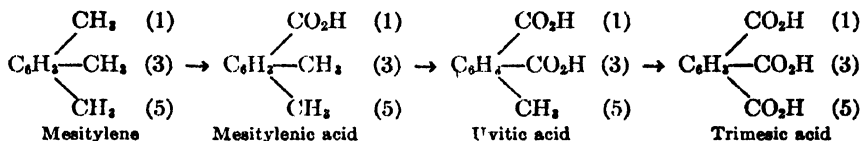
***p*-Xylene.**—*p*-Xylene is formed when camphor is distilled with  $\text{ZnCl}_2$ , and has been synthesised from *p*-bromotoluene, and from *p*-dibromobenzene by the action of methyl iodide and sodium (*Jannasch*, Ber. 10, 1355). On oxidation with nitric acid it first gives *p*-toluic acid, then terephthalic acid, and with  $\text{CrO}_3$ , terephthalic acid only. Electrochemical oxidation produces *p*-toluyl alcohol, *p*-toluyl aldehyde, and hydrotoluin,  $\text{MeC}_6\text{H}_4\text{CHOHCHOHC}_6\text{H}_4\text{Me}$  (*Fichter*, *Helv.* 9, 1097). It dissolves in fuming sulphuric acid forming a crystalline sulphonic acid. Its electric moment is zero.

**Ethyl-benzene**,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ , is also found in coal-tar, and is obtained from bromobenzene by the action of ethyl bromide and sodium, and from benzene by the action of ethyl bromide and aluminium chloride. It is also formed by the catalytic reduction of styrene,  $\text{PhCH}=\text{CH}_2$  (*Willstätter*, Ber. 46, 535). It is formed together with diphenyl-ethane by the action of vinyl chloride and aluminium chloride on benzene (*Davidson*, Am. 51, 2978). It can be prepared from benzene and ethylene under pressure with  $\text{BF}_3$  as catalyst, together with diethylbenzenes (*Patieff* and *Grosse*, Am. 58, 2339). It is oxidised by dilute nitric acid and by chromic acid to benzoic acid, and by  $\text{CrO}_2\text{Cl}_2$  to phenyl-acetaldehyde,  $\text{Ph}\cdot\text{CH}_2\cdot\text{CHO}$ .

**THE HYDROCARBONS,  $\text{C}_9\text{H}_{12}$ .** The isomeric relations between the eight compounds of this formula—the three trimethyl-benzenes, three methyl-ethyl-benzenes, and two propyl-benzenes—have been mentioned on p. 42. Their physical constants are given in the table on p. 42.

**Mesitylene**, *sym*-trimethyl-benzene, is found in coal-tar and in some fractions in the distillation of naphtha (*Konovalov*). Its formation from allylene or acetone under the influence of conc. sulphuric acid (*Lucas*, Ber. 29, 958, 2884), which was discussed on p. 25,

was discovered by *Kane* in 1837. For the preparation by means of this reaction see *Adams*, *Org. Synth.* 2, 41). HCl, at a temperature of 100–200°, and a pressure of 100 atm., has the same effect as sulphuric acid (*Ipatieff*, *Ber.* 63, 3072). The proof of its symmetrical structure (p. 12) has been a corner stone in establishing the orientation of many benzene substitution products. With dilute nitric acid mesitylene gives mesitylenic, uvitic, and trimesic acids.



With ozone mesitylene gives a triozone, which is decomposed by water with formation of methyl-glyoxal (*Harries*, *Ann.* 343, 370).

**Pseudocumene**, 1,3,1-trimethylbenzene, is also found in coal-tar. It is separated from mesitylene by means of its sparingly soluble sulphonic acid, from which it is regenerated (p. 40). It can be obtained from bromo-*p*-xylene and 4-bromo-*m*-xylene, which establishes its constitution.

**Hemimellitene**, 1,2,3-trimethylbenzene, is found in coal-tar (*Schultz*, *Ber.* 42, 3603), and is obtained from isodurylic acid,  $\text{C}_6\text{H}_2\text{Me}_3\text{CO}_2\text{H}$ , and from 2-bromo-*m*-xylene by the action of methyl iodide and sodium.

The three *ethyl-toluenes* are prepared from the three bromo-toluenes by the action of an ethyl halide and sodium. All three have been detected in coal-tar (*Schultz*, *ibid.* 3613).

*m*-Ethyl-toluene is formed when turpentine is passed over copper at 600° (*Mailhe*, *Bull.* 29, 290).

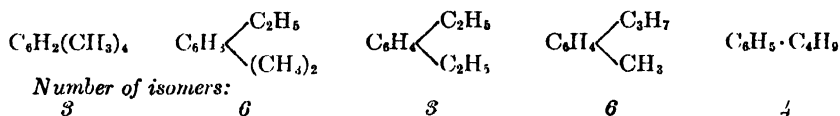
*p*-Ethyl-toluene has been obtained by reduction of *p*-methyl-styrene, *p*-cresyl-ketone, and methyl-*p*-tolyl-ketone (*Detresen*, *Ber.* 28, 2648; *Klages*, *Ber.* 36, 1637; *Auwers*, *Ann.* 419, 110).

***n*-Propyl-benzene** is obtained from bromobenzene by the action of *n*-propyl bromide or iodide and sodium, from benzyl chloride by the action of zinc diethyl, from benzene, *n*-propyl bromide and aluminium chloride at –2° (*Heise*, *Ber.* 24, 768), and also from propenyl-benzene,  $\text{PhCH}:\text{CHCH}_3$  by the action of sodium and alcohol (*Klages*, *Ber.* 36, 622). It is prepared from benzyl magnesium chloride by the action of diethyl sulphate (*Gillmann*, *Org. Synth.* 1, 458). It has been detected in coal-tar.

**Cumene**, isopropyl-benzene,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$ , first obtained from cuminic acid,  $\text{Me}_2\text{CHC}_6\text{H}_4\text{CO}_2\text{H}$ , by distilling with lime, has been synthesised from benzal chloride and zinc methyl, and from benzene and isopropyl chloride or bromide in the presence of aluminium chloride. If *n*-propyl bromide is used in the last reaction instead of the isopropyl compound, isopropyl-benzene is still formed, unless the reaction is carried out in the cold, because on heating, and in the presence of aluminium chloride, the *n*-propyl radical rearranges to isopropyl. The most convenient method of synthesis is the reduction of isopropenyl-benzene,  $\text{PhCMe}:\text{CH}_2$ , with sodium and alcohol (*Klages*, *Ber.* 35, 2640). It is formed, together with di- and

tri-isopropyl-benzenes, by the action of propylene on benzene in the presence of sulphuric acid or  $\text{BF}_3$  (*Wunderly*, Am. 58, 1007; *Ipatieff*, *ibid.* 58, 2339). In the animal organism cumene is oxidised to isopropyl-phenol (*Schotten*, Ber. 17, 2551).

**THE HYDROCARBONS,  $\text{C}_{10}\text{H}_{14}$ .** Theory predicts 22 isomers:



(a) The three possible tetramethylbenzenes,  $\text{C}_6\text{H}_2(\text{CH}_3)_4$ , are known.

**Durene**, 1,2,4,5- or *sym-tetramethylbenzene*, is found in coal-tar (*Schulze*, Ber. 18, 3034), and has been prepared by the following reactions: from 6-bromo-pseudocumene and from 4,6-dibromo-*m*-xylene by the action of methyl iodide and sodium; from toluene, xylene, or pseudocumene by the action of methyl chloride and aluminium chloride (*Smith*, Org. Synth. 10, 32); from *p*-xylene by the action of formaldehyde and  $\text{HCl}$  and reduction of the resulting dichloromethyl compound,  $\text{C}_6\text{H}_2[1,4]\text{Me}_2[2,5](\text{CH}_2\text{Cl})_2$ , with zinc dust and  $\text{NaOH}$  (*Braun*, Ber. 67, 1094); and from penta- and hexamethylbenzene by the action of  $\text{AlCl}_3$ . On oxidation it gives durylic acid and eumidic acid,  $\text{Me}_2\text{C}_6\text{H}_2(\text{CO}_2\text{H})_2$ , which establishes its symmetrical structure. Conc. sulphuric acid converts durene into hexamethylbenzene and the sulphonic acids of prehnitol, pseudocumene, and *m*-xylene, which can be separated by means of their amides. Pentamethyl- and penta-ethylbenzenes behave similarly (*Jacobsen*, Ber. 20, 896).

**Isodurene**, 1,2,3,5- or *unsym-tetramethylbenzene*, is obtained from bromomesitylene, methyl iodide, and sodium (*Jannasch*, Ber. 27, 3441), which establishes its constitution. It is formed when camphor is treated with zinc chloride or iodine (*Armstrong*, Ber. 16, 2259). On oxidation it gives 3-isodurylic acid, and finally prehnitic acid (p. 396) (*Jacobsen*, Ber. 15, 1853).

1,2,3,4- or *vic*-Tetramethylbenzene (often incorrectly called prehnitol) has been prepared from 2-bromo-pseudocumene and from 2,4-dibromo-*m*-xylene by the action of methyl iodide and sodium. On oxidation it gives a trimethylbenzoic acid,  $\text{C}_6\text{H}_2(\text{Me})_3\text{CO}_2\text{H}$ , and mellophanic acid,  $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$  (p. 396) (*Jacobsen*, Ber. 19, 1814; 21, 282).

(b) The dimethyl-ethyl-benzenes, 1,2,4- b.p.  $189^\circ$ , and 1,3,4- b.p.  $184^\circ$ , and 1,4,3- b.p.  $185^\circ$ , are formed when camphor is treated with  $\text{ZnCl}_2$  or iodine, and are obtained from the corresponding dimethyl-vinyl-benzenes by reduction. The 1,3,5-compound, b.p.  $185^\circ$ , has been prepared from acetone, and from methyl-ethylketone with  $\text{H}_2\text{SO}_4$  (*Klages*, Ber. 36, 1637; *Stahl*, Ber. 23, 988; *Uhlhorn*, *ibid.* 2344; *Tohl*, Ber. 25, 1533; *Anschutz*, Ber. 18, 666).

(c) The three diethyl-benzenes on oxidation give first ethyl-benzoic and then phthalic acids. *m*-Diethylbenzene is formed when ethylene is passed through benzene in the presence of aluminium chloride (*Copenhagen*, *Reid*, Am. 49, 3157). *p*-Diethylbenzene, b.p.  $183^\circ$ , has been obtained from *p*-ethylstyrene by reduction (*Klages*, Ber. 36, 1633).

(d) Methyl-*n*-propyl-benzenes: *o*- b.p.  $181^\circ$ , *m*- b.p.  $177^\circ$ , *p*- b.p.  $183^\circ$ , are prepared from *o*-, *m*-, and *p*-bromotoluene, *n*-propyl iodide and sodium (*Widmann*, Ber. 24, 443; *Tohl*, *ibid.* 1649; *Bayzac*, Ber. 29, R 417).

(e) Methyl-isopropyl-benzenes, *cymenes*. The most important of these is *p*-cymene. *m*-Methyl-isopropylbenzene or *m*-cymene is found in light resin oil (*Kelbe*, Ann. 210, 10), and is also obtained by heating fenchone with  $\text{P}_2\text{O}_5$  (*Wallach*, Ann. 275, 157). *o*-Cymene has been prepared from *o*-bromocumene by the action of sodium and methyl iodide (*Sprinkmeyer*, Ber. 34, 1950), and also from *o*- $\alpha$ -dimethylstyrene,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}:\text{CH}_2$ , by catalytic reduction.

The *o*- and *m*-cymenes have been obtained by dehydration of dimethyl-*o*- and *m*-tolyl-carbinols, with subsequent reduction (*Eisenlohr*, Ber. 57, 1808). All three isomers can be obtained by treating the corresponding toluic esters or methyl-acetophenones with an excess of magnesium methyl iodide. The *o*- and *p*-compounds are obtained, together with 2,4-di-isopropyl-toluene by direct introduction of the isopropyl group into toluene (*Dessaigue*, Bull. [5], 2, 617).

***p*-Cymene**, 1,4-methyl-isopropyl-benzene (see table on p. 42), is found, together with cuminic aldehyde, in Roman caraway oil from the seeds of *Cuminum cyminum*, in the oil from the seeds of cowbane, *Cicuta virosa*, in the oil from *Ptychotis ajowan*, in thyme oil, in eucalyptus oil from *Eucalyptus globulus*, and in many other essential oils. It is prepared from thymol, carvacrol, or camphor, by the action of  $P_2S_5$ . (*Armstrong*, Ber. 16, 2259) or  $P_2O_5$  (*Fittica*, Ann. 172, 307); from turpentine oil and other terpenes, by the removal of 2H by the action of  $H_2SO_4$  or  $I_2$ ; from dipentene and white camphor oil by treating with S in the presence of certain catalysts, particularly  $ZnCl_2$  (*Kimura*, J. Soc. Chem. Ind. Japan, 37, 1934). The formation of cymene on boiling cuminyl alcohol with zinc dust, and from citral (Vol. II, p. 204), and, in large quantities, in the manufacture of sulphite paper pulp and of xylose should be noted. The constitution of *p*-cymene was established by *Widman* (Ber. 24, 439, 970, 1362) by synthesis from *p*-bromo-isopropyl-benzene, methyl iodide and sodium. Cymene has a pleasant odour; its most characteristic derivative is barium cymene-sulphonate  $(C_{10}H_{13}SO_3)_2Ba + 3H_2O$ , which crystallises in shiny leaflets.

By the action of dilute  $HNO_3$  or of chromic acid cymene is oxidised to *p*-toluic and terephthalic acids, but in the animal organism, or on shaking with NaOH and air, it is oxidised to cuminic acid.  $KMnO_4$  gives *p*-(hydroxy-isopropyl)benzoic acid,  $(CH_3)_2C(OH)C_6H_4CO_2H$ , m.p. 155–156°, which loses water on treatment with HCl or  $H_2SO_4$ , loses water and gives *p*-isopropenylbenzoic acid, in two isomeric forms, m.ps. 160–161° and 255–260° (*Meyer*, Ann. 219, 282). The action of concentrated  $HNO_3$  on cymene produces *p*-tolyl-methyl-ketone (*Widman*, Ber. 19, 588; *Holleman*, Ber. 20, R373). The vapours are decomposed by activated Fuller's earth at 300–450°, into toluene and propylene (Ger. Pat. 483,640). With  $AlCl_3$  toluene and other hydrocarbons are formed (*Schorger*, Am. 39, 2671).

(f) **Butyl-benzenes**: *n*-Butyl-benzene, b.p. 180°. Isobutyl-benzene, b.p. 169°. sec.-Butyl-benzene, b.p. 174°, is obtained by reduction of sec.-butenylbenzene,  $Ph \cdot CMe \cdot CHCH_3$  (*Klages*, Ber. 35, 2642). Tert.-butyl-benzene, b.p. 168.7°. The latter is not attacked by bromine in sunlight in the cold (*Seukowski*, Ber. 29, 2412; *Baur*, Ber. 27, 1610). The introduction of butyl radicals into benzene can be best carried out with  $FeCl_3$  (*Noelting*, Chem. et Industrie 6, 719).

**Higher homologues of toluene.** Only the following compounds will be mentioned.

**THE HYDROCARBONS,  $C_{11}H_{14}$ .** Pentamethyl-benzene (see table, p. 42) is obtained together with hexamethylbenzene, from toluene, xylene, or mesitylene by the action of methyl chloride and aluminium chloride (*Jacobsen*, Ber. 20, 896), and from xylene *via* the trichloromethyl compound,  $C_6HMe_3(CH_2Cl)_3$  (*Braun*, Ber. 67, 1095). For its behaviour towards conc.  $H_2SO_4$ , see durene, p. 46.



**1,3,5-Diethylmethylbenzene**, b.p. 198–200°, is formed when a mixture of acetone and methyl-ethyl-ketone is treated with sulphuric acid. **1,2,4,5-Trimethyl-ethyl-benzene**, *ethyl-pseudo-cumene*, b.p. 207°. **Ethyl-mesitylene**, b.p. 208°. **1,3-Methyl-tert.-butyl-benzene**, b.p. 185–187°, occurs in resin oil obtained by the distillation of fir resin, and has been obtained from toluene and isobutyl bromide in the presence of aluminium chloride. Its trinitro-derivative is the artificial toluene-musk (p. 65). The isomeric **1,4-tert.-butyl-toluene**, m.p. 192–193° is obtained from toluene and isobutyl alcohol under the influence of fuming sulphuric acid. **Tert.-butyl-cymenes**, b.p. about 225°, are intermediate products in the preparation of an artificial musk (p. 65) (U. S. Pat. 1,951,123; *Thöl*, Ber. 25, 1530; *Klages*, Ber. 36, 1641). **Amyl-benzenes**, see *Konavolov*, C. 1899, I, 776; *Klages*, Ber. 35, 2644.

**THE HYDROCARBONS, C<sub>12</sub>H<sub>18</sub>. Hexamethyl-benzene** (see table, p. 42) is obtained by polymerisation of crotonylene under the influence of H<sub>2</sub>SO<sub>4</sub>, by heating xylidine hydrochloride with methyl alcohol to 300°, by passing the mixed vapours of methyl alcohol and acetone over heated alumina (*Reckleben*, Ber. 46, 2363), and by the methods mentioned under durene and pentamethyl-benzene. It is insoluble in sulphuric acid since it forms no sulphonic acid. Potassium permanganate oxidises it to benzene-hexacarboxylic acid (mellitic acid), C<sub>6</sub>(CO<sub>2</sub>H)<sub>6</sub>.

**p-Di-n-propyl-benzene**, b.p. 220–221°, has been prepared from *p*-dibromobenzene, and *p*-*n*-propyl-isopropyl-benzene, b.p. 212°, from cumyl chloride, ClCH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHMe<sub>2</sub>, and zinc diethyl. On oxidation with HNO<sub>3</sub>, both give *n*-propyl-benzoic acid, and an isomer of cuminic acid. **Propyl-mesitylene**, b.p. 221° (*Thöl*, Ber. 28, 2460), **isobutyl-mesitylene**, b.p. 228–230°, and **isoamyl-mesitylene**, b.p. 241–243°, are obtained by reduction of the corresponding acyl-mesitylenes (*Klages*, Ber. 37, 1715). **1,3,5-Triethyl-benzene**, b.p. 218°, is formed from methyl-ethyl-ketone by the action of H<sub>2</sub>SO<sub>4</sub>, and, together with **1,2,4-triethyl-benzene**, from benzene, ethyl chloride, and aluminium chloride. The sulphonic acid of the latter is more stable towards phosphoric acid, so that the two isomers can be separated. The 1,2,4-compound can also be obtained from diethyl-vinyl-benzene by reduction (*Klages*, Ber. 36, 1634; *J.* pr. 65, 394). **1,2,3,4-Tetra-ethyl-benzene**, b.p. 254°. **1,2,4,5-Tetra-ethyl-benzene**, m.p. 13°, b.p. 250° (*Klages*, Ber. 36, 1635). **Penta-** (see table, p. 42) and **hexa-ethyl-benzene** are obtained from benzene, ethyl bromide, or ether, and aluminium chloride (*Jacobsen*, Ber. 21, 2819; *Galle*, Ber. 16, 1745). For optically active **hexyl-benzenes**, PhCH<sub>2</sub>CH<sub>2</sub>CHMe·C<sub>6</sub>H<sub>5</sub>, b.p. 220°, and PhCHMe·CH<sub>2</sub>CHMe<sub>2</sub>, b.p. 197°, and **p-isopropyl-hexylbenzene**, C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CHMe·C<sub>6</sub>H<sub>5</sub>, b.p. 265°, see *Klages*, Ber. 37, 654, 2308; 38, 2313. **Heptyl-benzene**, PhCHMe·CH<sub>2</sub>CH<sub>2</sub>CHMe<sub>2</sub>, b.p. 245° (*Braun*, Ber. 45, 2180). **Tert.-p-butyl-ethyl-benzene**, b.p. 209–213°, is obtained from *p*-butyl-acetophenone (*Holleman*, Rec. 23, 225). **Tert.-p-dibutyl-benzene**, m.p. 76°, b.p. 236° (*Bödker*, Bull. [3], 31, 965). **Tert.-butyl-m** and **-p-cymenes**, b.ps. 227° and 228° (corr.), are obtained from the cymenes by the action of tert. butyl alcohol and H<sub>2</sub>SO<sub>4</sub> (*Barbier*, Helv. 15, 592). **Dimethyl-tert.-butyl-benzene**, b.p. 201–203°, is obtained from *m*-xylene and triisobutyl borate in the presence of AlCl<sub>3</sub> (Br. Pat. 367292).

The following mono- and di-alkyl benzenes with long side-chains have been prepared from bromobenzene and bromotoluene by Fittig's method (*Krafft*, Ber. 21, 3182; 29, 1326): **n-hexyl-benzene**, b.p. 224–228°, **n-heptyl-benzene**, b.p. 244–246°, **n-octyl-benzene**, b.p. 257°, **n-nonyl-benzene**, b.p. 98–100° (1 mm.) (*Weygand* and *Mensdorf*, Ber. 68, 1830), **cetyl-benzene**, C<sub>6</sub>H<sub>5</sub>·C<sub>18</sub>H<sub>35</sub>, m.p. 27°, b.p. 230° (15 mm.), **α-methyl-cetyl-benzene**, m.p. 8–9°, b.p. 239° (15 mm.), **m-methyl-cetyl-benzene**, m.p. 11–12°, b.p. 237° (15 mm.), **p-methyl-cetyl-benzene**, m.p. 27°, b.p. 240° (15 mm.), **octadecyl-benzene**, m.p. 36°, b.p. 249° (15 mm.). **Bornyl-benzene**, b.p. 117° (1.5 mm.), is obtained from bornyl chloride and benzene under the action of AlCl<sub>3</sub> (*Kamienski*, Roczn. Chem. 14, 1348; 15, 92).

## 2. HALOGEN DERIVATIVES OF THE BENZENE HYDROCARBONS

### Halogen Nuclear Substitution Products

Benzene, in sunlight, adds on six atoms of chlorine or bromine, forming *benzene hexachloride* and *benzene hexabromide*—substances which, as cyclohexane derivatives, have been dealt with in connection with that hydrocarbon (Vol. II, p. 92). The hydrogen atoms attached to the benzene nucleus are, however, easily *substituted* by chlorine and bromine, more readily, in fact, than the hydrogen atoms of paraffins.

*Properties and reactions.*—The halogen-substituted benzenes are colourless liquids or colourless crystalline substances. They have a faint, but not unpleasant odour. They are insoluble in water, but dissolve readily in organic solvents, and volatilise without decomposition. Of the dihalogen-substituted benzenes the para-compounds are solid at ordinary temperature; they melt at higher, but boil at lower temperatures than the *o*- and *m*-compounds.

The union between the halogen atoms and the benzene nucleus is remarkably stable. They react only with great difficulty with alkaline hydroxide (*Weber*, Ber. 18, 335; *Blau*, Mo. 7, 621; Ger. Pats. 249,939 and 269,542), ammonia, KCN, etc., quite unlike the alkyl halides (Vol. I, p. 162); but metals, such as magnesium, sodium, and copper remove halogen atoms, especially from bromo- and iodo-compounds. This is of importance in the synthesis of homologous benzene hydrocarbons (p. 38). Grignard compounds are readily formed by the action of magnesium, and are also important in synthesis. Chloro-, bromo-, and iodo-benzene react particularly readily with piperidine, *phenyl-piperidine* being formed. Prolonged heating with dimethylamine gives dimethylaniline (*Sellmann*, Ber. 21, 2279); *Menschutkin*, C. 1898, II, 478); cf. nitrohalogen-substituted benzenes, p. 62. Small quantities of powdered copper, or copper salts, which act catalytically, greatly facilitate the reaction with ammonia and amines (*Goldberg*, Ber. 40, 4541; Ger. Pat. 204,951). Sodium amalgam in alcohol, hydrogen iodide and phosphorus (*Monneyrol*, Bull. [3], 19, 554; *Klages*, J. pr. 65, 564), nickel and hydrogen at 270° (*Sabatier*, C.r. 138, 245), or catalytically activated hydrogen in solvents in the cold (*Rosenmund*, Ber. 51, 578) reduce the halogen-substituted benzenes to benzene hydrocarbons. When the monohalogen compounds are hydrogenated under pressure in presence of KOH, diaryls, and polyaryls are formed (*Busch and Weber*, J. pr. 146, 13). When their vapours mixed with hydrogen are passed over heated alkaline-earth phosphates or other catalysts, the halogen is replaced and phenols are obtained (U. S. Pat. 1,935,468). Phenol is also formed in good yield when chlorobenzene is heated with aqueous sodium hydroxide at 300° in an autoclave fitted with a stirrer (*Voroshzov*).

Fluorobenzenes are formed from benzene diazo-piperidides by the action of hydrofluoboric acid (*Wallach*, Ann. 243, 221):



They are formed from benzene-diazonium chlorides, sulphates, and fluorides (*q.v.*) by decomposition with aqueous hydrofluoric acid, or hydrofluoboric acid, or sodium fluoborate (Holleman, *Rec.* 24, 25, 140; Schiemann, *Ber.* 62, 3035). The best method is to precipitate the sparingly soluble diazonium borofluoride  $\text{ArN}_2\text{BF}_4$ ; the dry salt when heated decomposes smoothly into  $\text{BF}_3$  and the fluoro-compound (Balz, Schiemann, *Ber.* 60, 1186). For the action of fluorine on aromatic compounds see Bockemüller, *Ann.* 504, 34, 57.

**Fluorobenzene**,  $\text{C}_6\text{H}_5\text{F}$ , m.p.  $-39.2^\circ$ , b.p.  $85^\circ$ ,  $d_{20}^{20}$  1.0244, electric moment 1.4 D., has also been obtained by heating fluorobenzoic acid with HCl.

*o*-Difluorobenzene, m.p.  $-34^\circ$ , b.p.  $91-92^\circ$ , electric moment 2.38 D.; *m*-difluorobenzene, m.p.  $-59^\circ$ , b.p.  $82.8^\circ$ , from the diazophenylene-diamines by treating them with hydrofluoboric acid (Schiemann, *Ber.* 62, 3035); *p*-difluorobenzene, m.p.  $-13^\circ$ , b.p.  $88.5^\circ$ ,  $d_{18}^{18}$  1.173; dipole moment zero.

**Chlorobenzenes.** *Methods of formation*—(1) Free chlorine acts only slowly on benzene, but its action is catalysed by  $\text{I}_2$ ,  $\text{MoCl}_5$ ,  $\text{VCl}_4$  (Steele, *Proc.* 1903, 222),  $\text{FeCl}_3$  (Thomas, *C.r.* 128, 1576), or  $\text{AlCl}_3$ . The chlorine may be diluted with HCl gas (Fr. Pat. 480,151, add. 22,138). Chlorination can also be effected with  $\text{PbCl}_4 \cdot 2\text{NH}_4\text{Cl}$  (Seyewetz, *C.r.* 135, 1126).

(2) The hydroxyl group of phenols is replaced with difficulty by chlorine by the action of  $\text{PCl}_5$ ; this replacement occurs more readily in the nitrophenols.

(3) A very important method for preparing chlorobenzenes and aromatic halogen-substituted derivatives in general, is based on the reactions of the diazo-compounds, which are obtained from amino-compounds, the reduction products of nitro-compounds. The higher the atomic weight of the halogen, the more readily does the reaction take place. No atomic rearrangement is involved, the halogen taking the place previously occupied by the diazo, amino, or nitro-group (see p. 123). If, therefore, the constitution of one compound in a series of di- and poly-substitution products is known, the constitution of all of them can be arrived at.

In the electrolytic chlorination of benzene in a mixture of acetic acid and conc. HCl, chlorobenzene, *p*-dichlorobenzene, *as*-tetrachlorobenzene, chloranil, pentachlorophenol, and hexachlorobenzene are formed in succession. Toluene behaves similarly (Fichter, *Ber.* 49, 2473).

| Name and Formula                                                          | M.p.          | B.p.        | d.                   | $\mu$ |
|---------------------------------------------------------------------------|---------------|-------------|----------------------|-------|
| Monochlorobenzene $\text{C}_6\text{H}_5\text{Cl}$                         | $-45^\circ$   | $132^\circ$ | 1.128 ( $0^\circ$ )  | 1.55  |
| 1,2-( <i>o</i> -)Dichlorobenzene $\text{C}_6\text{H}_4\text{Cl}_2$        | $+16.7^\circ$ | $180^\circ$ | 1.293 ( $25^\circ$ ) | 2.25  |
| 1,3-( <i>m</i> -)Dichlorobenzene                                          | $-26.4^\circ$ | $172^\circ$ | 1.283 ( $25^\circ$ ) | 1.48  |
| 1,4-( <i>p</i> -)Dichlorobenzene                                          | $+53^\circ$   | $174^\circ$ | 1.226 ( $75^\circ$ ) | 0     |
| 1,2,3-( <i>v</i> -)Trichlorobenzene $\text{C}_6\text{H}_3\text{Cl}_3$     | $53^\circ$    | $218^\circ$ | .....                | ..    |
| 1,2,4-( <i>as</i> -)Trichlorobenzene                                      | $17^\circ$    | $213^\circ$ | 1.416 ( $21^\circ$ ) | ..    |
| 1,3,5-( <i>s</i> -)Trichlorobenzene                                       | $63.4^\circ$  | $208^\circ$ | .....                | 0     |
| 1,2,3,4-( <i>v</i> -)Tetrachlorobenzene $\text{C}_6\text{H}_2\text{Cl}_4$ | $46^\circ$    | $254^\circ$ | .....                | ..    |
| 1,2,3,5-( <i>as</i> -)Tetrachlorobenzene                                  | $51^\circ$    | $246^\circ$ | .....                | ..    |
| 1,2,3,5-( <i>s</i> -)Tetrachlorobenzene                                   | $140^\circ$   | $244^\circ$ | .....                | ..    |
| Pentachlorobenzene $\text{C}_6\text{HCl}_5$                               | $87^\circ$    | $276^\circ$ | .....                | ..    |
| Hexachlorobenzene $\text{C}_6\text{Cl}_6$                                 | $231^\circ$   | $326^\circ$ | .....                | ..    |

When chlorobenzene is further chlorinated, *p*-dichlorobenzene is the chief product, only a little *o*-dichlorobenzene being formed (Chattaway, *J.* 69, 848). *p*-Dichlorobenzene is also obtained from *p*-benzoquinone (*q.v.*), by the action of

$\text{PCl}_5$ . When *o*-, *m*-, and *p*-dichlorobenzenes are further chlorinated, 1,2,4-trichloro-, and 1,2,4,5-tetrachlorobenzenes are formed (*Cohen*, J. 87, 1360). The behaviour of the dichlorobenzenes on nitration is characteristic:

*o*-Dichlorobenzene gives 1,2-dichloro-4-nitrobenzene, m.p.  $43^\circ$ .  
*m*-Dichlorobenzene gives 1,3-dichloro-4-nitrobenzene, m.p.  $42^\circ$ .  
*p*-Dichlorobenzene gives 1,4-dichloro-3-nitrobenzene, m.p.  $55^\circ$ .

For the formation of highly chlorinated cyclohexanes in the chlorination of trichlorobenzenes, see *van der Linden*, Rec. 55, 315.

**Hexachlorobenzene**, *Julin's carbon chloride*, is often obtained when alkylbenzenes, and other benzene derivatives are exhaustively chlorinated. It is formed on passing chloroform or  $\text{C}_2\text{Cl}_4$  through a red-hot tube.

**BROMOBENZENES**. These compounds are obtained by the same methods as the chloro-compounds: 1. By direct substitution in the presence of bromine carriers, such as Fe,  $\text{AlBr}_3$ , or a mixture of  $\text{S}_2\text{Br}_2$  and  $\text{HNO}_3$  (*Edinger*, Ber. 33, 2883; *Stark*, Ber. 43, 672; *Datta*, Am. 38, 2543). 2. From diazo-compounds (p. 123).

| Name and Formula                                                         | M.p.           | B.p.            | d.                              | $\mu$ |
|--------------------------------------------------------------------------|----------------|-----------------|---------------------------------|-------|
| Monobromobenzene $\text{C}_6\text{H}_5\text{Br}$                         | $-31^\circ$    | $156^\circ$     | 1.517 ( $0^\circ$ )             | 1.56  |
| 1,2-( <i>o</i> -)Dibromobenzene $\text{C}_6\text{H}_4\text{Br}_2$        | $+7.8^\circ$ * | $225^\circ$     | 1.977 ( $17^\circ$ )            | 2.0   |
| 1,3-( <i>m</i> -)Dibromobenzene                                          | $-6.5^\circ$ * | $219.4^\circ$ * | 1.960 ( $16^\circ$ )            | 1.5   |
| 1,4-( <i>p</i> -)Dibromobenzene                                          | $89^\circ$     | $219^\circ$     | 1.832 ( $100^\circ$ )           | 0     |
| 1,2,3-( <i>v</i> -)Tribromobenzene $\text{C}_6\text{H}_3\text{Br}_3$     | $87.8^\circ$   | $\therefore$    |                                 |       |
| 1,2,4-( <i>as</i> -)Tribromobenzene                                      | $44^\circ$     | $275^\circ$     |                                 |       |
| 1,3,5-( <i>s</i> -)Tribromobenzene                                       | $122^\circ$    | $271^\circ$     |                                 |       |
| 1,2,3,4-( <i>v</i> -)Tetrabromobenzene $\text{C}_6\text{H}_2\text{Br}_4$ | $\therefore$   | $\therefore$    |                                 |       |
| 1,2,3,5-( <i>as</i> -)Tetrabromobenzene                                  | $98^\circ$     | $329^\circ$     |                                 |       |
| 1,2,4,5-( <i>s</i> -)Tetrabromobenzene                                   | $180^\circ$    | $\therefore$    |                                 |       |
| Pentabromobenzene $\text{C}_6\text{HBr}_5$                               | $160^\circ$    | $\therefore$    |                                 |       |
| Hexabromobenzene $\text{C}_6\text{Br}_6$                                 | $316^\circ$    | $\therefore$    | <i>Eckert</i> , J. pr. 102, 362 |       |

\* Private communication of *W. Körner*.

The dibromobenzene obtained by bromination of hot benzene is chiefly the *p*-compound, with some ortho (*Holleman*, Ber. 10, 1345). The behaviour of the dibromobenzenes when nitrated is characteristic, as with the dichlorobenzenes.

The production of *tribromobenzenes* from the three dibromobenzenes has been used for determining the constitution of all these compounds (*Körner*; see p. 11). **Hexabromobenzene** is produced by heating  $\text{CBr}_4$  at  $300^\circ$ . For **chlorobromobenzenes** see *Thomas*, Bull. [3] 21, 181; *Noneyrat*, C.r. 129, 605; *Hurtley*, J. 79, 1293; *Holleman*, Rec. 30, 305; *Norbult*, Ber. 52, 1031.

**IODOBENZENES** are obtained: 1. By *Kekulé's method*, by heating benzene, iodine, and iodic acid at  $200^\circ$  (Ann. 137, 161): The reaction is represented by the equation:



2. By treating benzene with a mixture of  $\text{S}_2\text{I}_2$  and  $\text{HNO}_3$ ; the latter has a dissociating effect on the sulphur iodide (*Edinger*, Ber. 33, 2875).

3. More often, iodobenzenes are prepared from amino-compounds via the diazo-compounds (p. 123).

4. Bromobenzene may be converted into iodobenzene by forming the Grignard compound,  $\text{PhMgBr}$ , and then treating it with iodine (*Bodroux*, C.r. 135, 1350).

| Name                                     | Formula                          | M.p.                          | B.p.        | $\mu$ |
|------------------------------------------|----------------------------------|-------------------------------|-------------|-------|
| Iodo-benzene                             | $\text{C}_6\text{H}_5\text{I}$   | $-28.5^\circ$                 | $188^\circ$ | 1.25  |
| 1,2-( <i>o</i> -)Di-iodo-benzene         | $\text{C}_6\text{H}_4\text{I}_2$ | $+27^\circ$                   | $286^\circ$ | 1.27  |
| 1,3-( <i>m</i> -)Di-iodo-benzene         | ..                               | $34^\circ$                    | $285^\circ$ | 1.69  |
| 1,4-( <i>p</i> -)Di-iodo-benzene         | ..                               | $129^\circ$                   | $285^\circ$ | 0     |
| 1,2,3-( <i>v</i> -)Tri-iodo-benzene      | $\text{C}_6\text{H}_3\text{I}_3$ | $116^\circ$                   |             |       |
| 1,2,4-( <i>as</i> -)Tri-iodo-benzene     | ..                               | $91.4^\circ$                  |             |       |
| 1,3,5-( <i>s</i> -)Tri-iodo-benzene      | ..                               | $184.2^\circ$                 |             |       |
| 1,2,3,4-( <i>v</i> -)Tetra-iodo-benzene  | $\text{C}_6\text{H}_2\text{I}_4$ | $136^\circ$                   |             |       |
| 1,2,4,6-( <i>as</i> -)Tetra-iodo-benzene | ..                               | $148^\circ$                   |             |       |
| 1,2,4,5-( <i>s</i> -)Tetra-iodo-benzene  | ..                               | $254^\circ$                   |             |       |
| Penta-iodo-benzene                       | $\text{C}_6\text{HI}_5$          | $172^\circ$                   |             |       |
| Hexa-iodo-benzene                        | $\text{C}_6\text{I}_6$           | $340^\circ\text{--}350^\circ$ |             |       |

**HEXAIODOBENZENE**,  $\text{C}_6\text{I}_6$ , is produced by the exhaustive iodination of benzene-carboxylic acids (benzoic acid, terephthalic acid) with iodine and fuming sulphuric acid. It forms reddish-brown needles which melt and decompose at  $340\text{--}350^\circ$  (*Rupp*, Ber. 29, 1631; *Durand, Mancet*, Bull. [5] 2, 665).

1,3,5-Tri-iodo-2-chlorobenzene (*Green*, Am. Chem. J. 36, 600). For bromiodobenzenes, see *Hirtz*, Ber. 29, 1405; *Narbutt*, Ber. 52, 1032; *Datta*, Am. 41, 287, 292. 1,3,5-Tri-iodo-2,4,6-tribromobenzene,  $\text{C}_6\text{Br}_3\text{I}_3$ , m.p.  $322^\circ$ , see *Istrati*, C.r. 127, 519.

**IDOCHLORIDES. IOSOBENZENE. IODOXYBENZENE. DIPHENYLIODONIUM HYDROXIDE.** Iodobenzene and its homologues are converted by the action of chlorine, or of substances readily liberating chlorine, into *iodochlorides*, such as phenyl iodochloride,  $\text{PhICl}_2$  (*Willgerodt*, 1886). In these compounds, chlorine is linked to iodine, as in iodine trichloride,  $\text{ICl}_3$ . The formation of these interesting compounds serves to characterise the iodinated benzene derivatives.

The iodochlorides are readily converted into *iodosobenzenes*, e.g.,  $\text{PhIO}$ , and should be regarded as chloro-anhydrides of the latter. These on oxidation give *iodoxybenzenes*, e.g.,  $\text{PhIO}_2$ . Finally, from iodoso- and iodoxy-benzene, *diphenyl-iodonium hydroxide*, a strong base, is obtained.

**Phenyl iodochloride**,  $\text{PhICl}_2$ , yellow needles, is formed when chlorine is passed into a solution of iodobenzene in chloroform. When heated or exposed to light, it loses  $\text{HCl}$  and  $\text{Cl}_2$  and gives *p*-iodochlorobenzene and iodobenzene (*Caldwell*, J. 91, 240, 528; *Zappi*, Bull. 1929, 45, 848). When shaken with water and alkali, or other bases, it gives iodosobenzene:



For other reactions of phenyl iodochloride see *Zappi*, Bull. 1930, 47, 612.

**Iodosobenzene**,  $\text{PhIO}$ , is an amorphous substance, exploding at about  $210^\circ$ . On treatment with acidified  $\text{KI}$  it gives up its oxygen, with liberation of an equivalent quantity of iodine:



It behaves somewhat like a base, and gives salts derived from the hypothetical hydrate  $\text{PhI}(\text{OH})_2$ .

**Iodoxybenzene**,  $\text{PhIO}_2$ , is formed by a disproportionation reaction when iodosobenzene is heated alone or boiled with water:



It is also formed by oxidising iodosobenzene with  $\text{HOCl}$ , phenyl iodochloride with bleaching powder solution, or iodobenzene itself with potassium persulphate and conc.  $\text{H}_2\text{SO}_4$  (Caro's reagent) (*Willgerodt*, Ber. 29, 1567; 33, 853; *Bamberger*, Ber. 33, 533). Iodoxybenzene explodes at  $227-228^\circ$ . With conc. hydrofluoric acid it gives benzeneiodoxy-fluoride,  $\text{PhIOF}_2$ , which regenerates iodoxybenzene when treated with water (*Weinland*, Ber. 34, 2631).

4-Nitro-iodoxybenzene explodes at  $212-213^\circ$ , and is obtained by heating 4-nitro-iodobenzene with water together with 4-nitro-iodobenzene (*Willgerodt*, Ber. 26, 1808).

2,4-Dinitro-iodoxybenzene, explodes at  $140-160^\circ$ , and is obtained by the action of  $\text{HOCl}$  in glacial acetic acid on 2,4-dinitro-iodobenzene. For the reactions of both compounds with  $\text{AgNO}_3$ ,  $\text{HCl}$ , etc., see *Vorländer*, Rec. 48, 912; Ber. 70, 146, 151.

Diphenyl-iodonium hydroxide,  $\text{Ph}_2\text{IOH}$ , is known only in aqueous solution. It is obtained by shaking a mixture of iodoso- and iodoxy-benzene with moist silver oxide, the equation being:

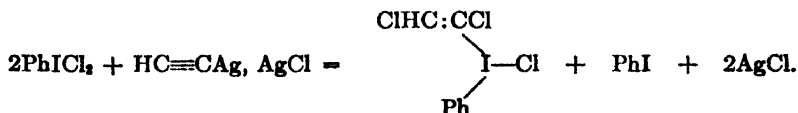


The oxygen atom in iodoso-benzene is exchanged for a phenyl group of iodoxy-benzene and  $\text{Ph}_2\text{I}^+$  and  $\text{IO}_2^-$  are formed. In this way iodoxybenzene can serve as a carrier of phenyl groups, as can  $\text{PhMgBr}$ , e.g., for transforming  $\text{HgO}$  into  $\text{PhHgOH}$  (*Nesmejanov*, Ber. 66, 199).

Diphenyl-iodonium hydroxide is strongly alkaline and forms true salts, such as  $\text{Ph}_2\text{I} \cdot \text{I}$ ,  $\text{Ph}_2\text{I} \cdot \text{Cl}$ ,  $\text{Ph}_2\text{I} \cdot \text{NO}_3$ , which resemble those of thallium. The carbonate and the nitrate are very soluble, but the chloride and the bromide are white insoluble substances.

Diphenyl-iodonium iodide,  $\text{Ph}_2\text{I} \cdot \text{I}$ , is formed from the cation  $\text{Ph}_2\text{I}^+$  with  $\text{I}^-$ , or by boiling iodoxy-benzene with aqueous  $\text{KI}$  (*Willgerodt*, Ber. 29, 2008). It is dimeric with iodobenzene. It forms yellow needles, sparingly soluble in alcohol. It melts at  $175-176^\circ$ , iodobenzene being formed (*V. Meyer*, Ber. 27, 1592). For the ease of exchange of the two iodine atoms see *Juliusberger*, *Topley*, *Weiss*, J. 1935, 1295.

Alkyl-aryl iodonium salts are obtained by the interaction of acetylene-silver chloride with aromatic iodo-chlorides:



Dichloro-vinyl-phenyl-iodonium chloride, m.p.  $174^\circ$ . The bromide decomposes at  $163^\circ$ . The free base is unstable (*Thiele*, Ann. 369, 132). Many homologous and substituted iodochlorides, iodoso- and iodoxy-benzenes, and iodonium hydroxides have been prepared (see *Willgerodt*, Ber. 39, 269 et al.).

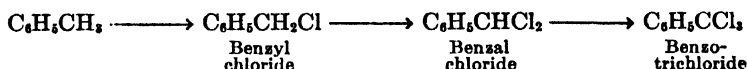
### Halogen Derivatives of the Alkyl Benzenes

Under the same conditions as with benzene itself, namely, in the cold, and in presence of halogen carriers ( $\text{I}_2$ ,  $\text{MoCl}_5$ ,  $\text{VCl}_5$ ,  $\text{FeCl}_3$ ,

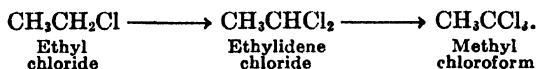
sulphur bromide, or bromine and nitric acid), chlorine and bromine substitute almost solely in the benzene nucleus of the alkyl-benzenes, and aromatic substitution products are formed. Thus, toluene yields:



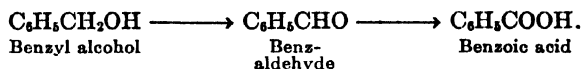
When, however, chlorine and bromine are passed into boiling alkyl-benzenes, the side-chain hydrogen only is replaced, and aliphatic substitution products are formed. Thus, toluene yields:



corresponding to:



These will be dealt with in connection with the corresponding oxygen-containing compounds:



In sunlight chlorine and bromine substitute in the side chains of the lower homologues, even in the cold (*Koczyński*, *Ber.* 35, 868). Isopropyl-benzene at the boiling point is converted by chlorine into *p*-chloro-isopropyl-benzene (*Genevresse*, *Bull.* [3], 9, 219).  $\text{PCl}_5$  also attacks the alkyl-groups of alkyl-benzenes when hot.

Nuclear substituted alkyl-benzenes can be obtained from the corresponding diazo-compounds.

Substitution can, of course, be effected both in the aromatic and the aliphatic residue of an alkyl-benzene. The halogen atoms entering the side-chain are reactive, and can readily be replaced by organic radicals, while the halogen atoms entering the benzene nucleus are very firmly bound. Aromatic monohalogen derivatives of alkyl-benzenes, especially bromoalkyl-benzenes, are often used for synthesising higher alkyl-benzenes by Fittig's method (p. 35). Oxida-

| Compound                       |                                                  | M.p.    | B.p.   | $\mu$ |
|--------------------------------|--------------------------------------------------|---------|--------|-------|
| 1,2-( <i>o</i> -)Fluorotoluene | $\text{CH}_3[1]\text{C}_6\text{H}_4[2]\text{Fl}$ | ..      | 114°   |       |
| 1,3-( <i>m</i> -)Fluorotoluene | $\text{CH}_3[1]\text{C}_6\text{H}_4[3]\text{Fl}$ | -110.8° | 116°   |       |
| 1,4-( <i>p</i> -)Fluorotoluene | $\text{CH}_3[1]\text{C}_6\text{H}_4[4]\text{Fl}$ | ..      | 117°   |       |
| 1,2-( <i>o</i> -)Chlorotoluene | $\text{CH}_3[1]\text{C}_6\text{H}_4[2]\text{Cl}$ | -34°    | 159.5° | 1.35  |
| 1,3-( <i>m</i> -)Chlorotoluene | $\text{CH}_3[1]\text{C}_6\text{H}_4[3]\text{Cl}$ | -48°    | 161.6° | 1.75  |
| 1,4-( <i>p</i> -)Chlorotoluene | $\text{CH}_3[1]\text{C}_6\text{H}_4[4]\text{Cl}$ | +7.5°   | 162.3° | 1.9   |
| 1,2-( <i>o</i> -)Bromotoluene  | $\text{CH}_3[1]\text{C}_6\text{H}_4[2]\text{Br}$ | -26°    | 179°   |       |
| 1,3-( <i>m</i> -)Bromotoluene  | $\text{CH}_3[1]\text{C}_6\text{H}_4[3]\text{Br}$ | -40°    | 184°   |       |
| 1,4-( <i>p</i> -)Bromotoluene  | $\text{CH}_3[1]\text{C}_6\text{H}_4[4]\text{Br}$ | 28°     | 184.6° |       |
| 1,2-( <i>o</i> -)Iodotoluene   | $\text{CH}_3[1]\text{C}_6\text{H}_4[2]\text{I}$  | ..      | 204°   |       |
| 1,3-( <i>m</i> -)Iodotoluene   | $\text{CH}_3[1]\text{C}_6\text{H}_4[3]\text{I}$  | ..      | 204°   |       |
| 1,4-( <i>p</i> -)Iodotoluene   | $\text{CH}_3[1]\text{C}_6\text{H}_4[4]\text{I}$  | 34°     | 213.5° |       |

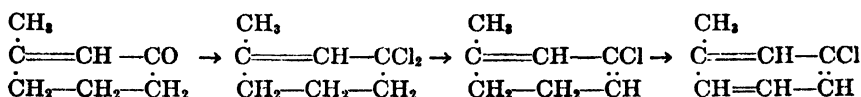
tion of the side chains to carboxyl groups serves to establish the constitution, and, at the same time, to determine the number of halogen atoms in the side chains.

The halogens can be replaced by hydrogen by the action of sodium amalgam and alcohol, hydrogen iodide, or hydrogen in the presence of catalysts.

The simplest representatives of the very numerous halogen substitution products of alkyl-benzenes, the monohalogeno-toluenes, are given in the table on page 54.

The *o*-, *m*-, and *p*-fluorotoluenes have been prepared by the same methods as fluorobenzene. On chlorinating or brominating toluene in the cold, or in the presence of iodine or ferric chloride, *p*- and *o*-compounds are produced in nearly equal quantities. *p*-Chlorotoluene is separated from the *o*-compound by heating at 180° with sulphuric acid, when the *o*-compound forms a sulphonic acid.

All the monochloro-, monobromo-, and moniodo-toluenes have been prepared in the pure state from the three toluidines by means of the diazo-compounds. The *o*- and *p*-chlorotoluenes are readily accessible from the corresponding toluidines. For the chlorination of toluene in the nucleus, and in the side chain see *Wertyporoch*, Ann. 493, 153. *m*-Bromotoluene has also been obtained by brominating aceto-*p*-toluidide to *m*-bromoaceto-*p*-toluidide, and then replacing the amino-group by hydrogen. *m*-Chlorotoluene has been obtained from 3-methyl- $\Delta^2$ -cyclohexenone (Vol. II, p. 115), which is easily prepared from methylenediacetoacetic ester. In this process the action of  $\text{PCl}_5$  first produces tetrahydro-*m*-dichlorotoluene, which then decomposes into  $\text{HCl}$  and dihydro-*m*-chlorotoluene. Bromine removes two hydrogen atoms from this compound, and *m*-chlorotoluene is obtained (*Klages*, Ber. 27, 3013).



From ethylidene-*bis*-acetoacetic ester, 1,3,5-chloro-*m*-xylene is obtained, and 1,3,6-chlorocymene has been similarly prepared from menthone, or keto-hexahydro-*p*-cymene (*Klages*, Ber. 29, 310, 314).

The iodoso- and iodoxy-compounds derived from *p*-iodotoluene are known (*Willgerodt*, Ber. 26, 358; 27, 1903).

The conversion of the halogen compounds of toluene to solid nitro-halogeno-toluenes, and their oxidation to halogenobenzoic acids of known constitution, has been used for their characterisation. Chromic acid oxidises *m*- and *p*-halogeno-toluenes to the corresponding carboxylic acids, but the ortho-compounds are oxidised to  $\text{CO}_2$ . With boiling dilute nitric acid, or with  $\text{KMnO}_4$ , or  $\text{K}_3\text{Fe}(\text{CN})_6$ , all three isomers are converted into carboxylic acids.

Six isomers of aromatic dihalogeno-toluenes with two similar halogens are possible. The six isomeric dichlorotoluenes are known (*Wynne*, Proc. 1895, 151); they are isomeric with benzal chloride,  $\text{PhCHCl}_2$ , and the three chlorobenzyl chlorides,  $\text{ClC}_6\text{H}_4\text{CH}_2\text{Cl}$ . For details of the higher chlorination products of toluene see *Cohen*, J. 81, 1324; 85, 1274; for the chlorination of cymene see *Tschernasheikov*, C. 1932, II, 1815. The six isomeric dibromotoluenes and diiodotoluenes are also known (*Wheeler*, Am. Chem. J. 42, 441). Pentabromotoluene has been obtained from cycloheptane (Vol. II, p. 70) and bromine. The six isomeric tribromoxylens are all known (*Jaeger*, Rec. 25, 352).

For fluorinated 1,2- and 1,4-dichlorobenzenes, see *Kraay*, Rec. 43, 1055; *de Crauw*, *ibid.* 1061; for the chlorination of monobromotoluene and the bromination of chlorotoluenes, and for di- and tribromotoluenes see *Cohen*, J. 105, 501, 1907; for chlorination of cumene see *Qrist and Salo*, C. 1936, I, 539, of *p*-cymene, *Qrist and Holmberg*, C. 1936, II, 1906, halogenation of the two latter hydrocarbons, *Varma and Srinivasan*, J. Ind. Chem. Soc. 13, 189.



| Compound                                              | M.p.     | B.p.     |
|-------------------------------------------------------|----------|----------|
| 1,2,4-Bromo- <i>o</i> -xylene.....                    | - 0.2°   | 214°     |
| 1,3,4-Bromo- <i>m</i> -xylene.....                    | ..       | 207°     |
| 1,4,2-Bromo- <i>p</i> -xylene.....                    | + 9°     | 205.5°   |
| Tribromo-hemimellithene (p. 45) .....                 | 245°     | ..       |
| 1,2,4,3-Monobromo-pseudocumene (p. 45).....           | ..       | 226-229° |
| 1,2,4,5,6-Dibromo-pseudocumene.....                   | 64°      | 293°     |
| Tribromo-pseudocumene .....                           | 229-230° | ..       |
| Monobromo-mesitylene (p. 44).....                     | - 1°     | 230-233° |
| Dibromo-mesitylene.....                               | +64°     | 276-278° |
| Tribromo-mesitylene.....                              | 224°     | ..       |
| Monobromo- <i>v</i> -tetramethylbenzene (p. 46) ..... | 30°      | 265°     |
| Dibromo- <i>v</i> -tetramethylbenzene .....           | 205°     | ..       |
| Monobromo-isodurene (p. 46).....                      | ..       | 253°     |
| Dibromo-isodurene.....                                | 209°     | ..       |
| Monobromo-durene (p. 46).....                         | 61°      | 262°     |
| Dibromo-durene.....                                   | 202°     | 317°     |
| Bromo-pentamethylbenzene.....                         | 160°     | 289°     |

The table above gives the bromo-derivatives of polymethyl-benzenes which are readily accessible.

Concentrated sulphuric acid has the remarkable capacity of transferring bromine atoms (like alkyl groups, see p. 39) from one position in the molecule to another; thus, monobromodurene is converted into a mixture of dibromodurene and durene.

A number of iodo-alkylbenzenes have been prepared by means of sulphur iodide and nitric acid in a manner similar to iodobenzene (Ber. 33, 2875). They give, like the latter, compounds in which iodine is polyvalent (A. 385, 328).

### 3. NITROGEN DERIVATIVES OF BENZENE HYDROCARBONS IN WHICH NITROGEN IS DIRECTLY LINKED TO THE RING

These compounds may be classified according to the number of nitrogen atoms contained in the substituent. The first class comprises compounds with only one nitrogen atom in each substituent and the first group to be discussed are the *nitro-compounds* which are so characteristic of the benzene derivatives. They are the starting point in the preparation of compounds of the groups which follow. Next come the *amino-compounds*, which are used for the preparation of many dyestuffs, and substances of importance in medicine. A link between the two groups is provided by the *nitroso-* and  *$\beta$ -hydroxyl-amino-compounds*.

The second class comprises compounds in which the nitrogen-containing substituent has two or more nitrogen atoms linked together. The *nitro-amines*, *nitroso- $\beta$ -hydroxylamines*, *nitrosamines*, *azoxy-compounds*, *hydrazines*, *diazo-* and *azo-compounds* contain two nitrogen atoms. The *nitroso-hydrazines*, *diazoamino-compounds*, and the *azoimino-compounds* have three nitrogen atoms. The *diazo-hydrazines* or *buzylene compounds* and the *tetrazines* have four nitrogen atoms. The *bis-diazo-amino-compounds* have five, and the *bis-diazo-tetrazines* or *octazenes* have eight nitrogen atoms.

Our knowledge of some of these classes of compounds has also been of great importance in connection with the chemistry of inorganic

nitrogen compounds. If these nineteen groups of aromatic nitrogen compounds are assumed to be derived from analogous hydrogen compounds in which the aromatic residues are replaced by hydrogen atoms, then of the nineteen hydrogen compounds, only six are known in the free state or as inorganic compounds, and these are printed in heavy type in the following list:

| Compounds                                            | Derived from                                |
|------------------------------------------------------|---------------------------------------------|
| 1. <i>Nitro</i> -compounds.....                      | <b>H·NO<sub>2</sub></b>                     |
| 2. <i>Nitroso</i> -compounds.....                    | <b>H·NO</b>                                 |
| 3. <i>β-Hydroxylamine</i> -compounds.....            | <b>H·NHOH</b>                               |
| 4. <i>Amino</i> -compounds.....                      | <b>H·NH<sub>2</sub></b>                     |
| 5. <i>Nitro-amines</i> .....                         | <b>H·NH·NO<sub>2</sub></b>                  |
| 6. <i>Nitroso-β-hydroxylamines</i> .....             | <b>H·N(OH)·NO</b>                           |
| 7. <i>Nitrosamines</i> .....                         | <b>H·NH·NO</b>                              |
| 8. <i>Diazo</i> -compounds.....                      | <b>H·N=N·OH or<br/>H·NH·NO or [H·N:N]OH</b> |
| 9. <i>Azo</i> -compounds.....                        | <b>H·N=N·H</b>                              |
| 10. <i>Azoxy</i> -compounds.....                     | <b>H·N(O):N·H</b>                           |
| 11. <i>Hydrazines</i> .....                          | <b>H·NH·NH<sub>2</sub></b>                  |
| 12. <i>Nitroso-hydrazines</i> .....                  | <b>H·N(NO)·NH<sub>2</sub></b>               |
| 13. <i>Diazo-amino</i> -compounds.....               | <b>H·N=N·NH<sub>2</sub></b>                 |
| 14. <i>Diazo-hydroxy-amino</i> -compounds.....       | <b>H·N=N·NHOH</b>                           |
| 15. <i>Azides. Diazo-imino</i> -compounds.....       | <b>HN<sub>3</sub></b>                       |
| 16. <i>Diazo-hydrazo- or Buzylene</i> compounds..... | <b>H·N=N·NH·NH<sub>2</sub></b>              |
| 17. <i>Tetrazenes</i> .....                          | <b>H·NH·N=N·NH<sub>2</sub></b>              |
| 18. <i>Bis-diazo-amino</i> -compounds.....           | <b>H·N=N·NH·N=N·H</b>                       |
| 19. <i>Bis-diazo-tetrazenes or Octazenes</i> .....   | <b>H·N:N·NH·N:N·NH·N:NH</b>                 |

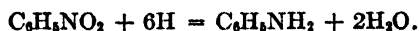
The first three groups will be dealt with in the order shown, but the remainder have been arranged according to their genetic rather than their systematic relationships as follows: nitroso-*β*-hydroxylamines (6); amino-compounds (4); nitramines (5); diazo-compounds (8); diazo-amino (13), bis-diazoamino (18), diazohydroxyamino (14), diazoimino-compounds (15); azoxy- and azo-compounds (10, 9); hydrazines (11), nitrosohydrazines (12), tetrazenes (17); diazo-hydrazo- or buzylene compounds (16); bis-diazotetrazenes, or octazenes (19).

#### (a) Nitro-derivatives of Benzene and the Alkyl-benzenes

Benzene and those alkyl-benzenes which contain hydrogen atoms attached to the ring readily give nitro-derivatives by the action of nitric acid:



In these compounds, which have a more or less pronounced yellow colour, the nitrogen of the nitro-group is directly linked with a carbon atom, just as in nitromethane, since, on reduction, amino-compounds are formed:



In the previous section it was stated that all the hydrogen atoms of

benzene could be replaced by Cl or Br. This is not so in the case of nitro-groups. The first two nitro-groups enter readily, but the third with difficulty, and it has not yet been possible to introduce directly more than three nitro-groups into a benzene derivative. The reason for this is the deactivation of the nucleus for substitution by the nitro-groups already present (see p. 24).

A mixture of one part of nitric acid and two parts of sulphuric acid acts more vigorously than nitric acid alone, because the sulphuric acid absorbs water, and by this means di- and tri-nitro products can be obtained. For more easily controlled nitration the substance is dissolved in glacial acetic acid or chloroform (*Willstätter*, Ber. 42, 4151). The more alkyl groups present in an aromatic hydrocarbon, the more readily is it nitrated. Nitrophenols are sometimes formed in small quantity in the nitration of aromatic hydrocarbons (*Armstrong*, Proc. 1891, 87; *Willstätter*, loc. cit.). On heating alkyl-benzenes with dilute nitric acid, the nitro-group may enter the aliphatic side-chain to some extent. The compounds so formed will be dealt with later in connection with the corresponding alcohols (*Konavalov*, Ber. 27, R 193).

Benzoyl and acetyl nitrates (p. 298) have been found to be excellent nitrating agents in certain cases (*Francis*, Ber. 39, 3798; *Pictet*, C.r. 144, 210). This has been held to be due to the fact that no water is formed in the reaction



while nitration with nitric acid gives rise to water. On the other hand, when *o*- and *p*-directing groups are present in the ring, the proportions of the two isomeric products is often very different with the acyl nitrates and nitric acid.

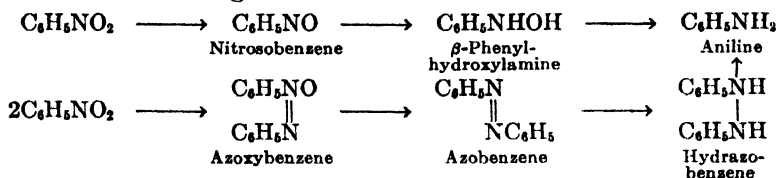
The action of  $\text{AlCl}_3$  on a mixture of a hydrocarbon with ethyl nitrate on certain inorganic nitrates, e.g.,  $\text{Cu}(\text{NO}_3)_2$ , dissolved in acetic anhydride and glacial acetic acid, may also give rise to nitro-compounds (*Boedtker*, Bull. 3, 726). The reaction takes place more readily in the presence of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  (*Menke*, Rec. 44, 141, 269). For  $\text{N}_2\text{O}_4$  as a nitrating agent see *Schaarschmidt*, Ber. 57, 32.

Aromatic nitro-compounds can be obtained from the corresponding amines by diazotisation followed by treatment with nitrous acid in presence of finely divided cuprous oxide. The reaction is the converse of the more usual procedure (nitro-compound  $\rightarrow$  amine), and is useful in cases where the amino-group can be introduced into a desired position, but the nitro-group cannot by any direct means. In some cases nitro-compounds have been obtained by direct oxidation of amines, e.g., nitrobenzene from aniline by oxidation with potassium permanganate, or permonosulphuric acid;  $\beta$ -phenylhydroxylamine (p. 69) and nitrosobenzene (p. 67) have been isolated as intermediate products (*Bamberger*, Ber. 32, 1675). The rate of nitration of a number of aromatic hydrocarbons has been determined. If the rate for toluene is taken as unity, that of *o*-xylene is 1.6–1.9, of *m*-xylene, 4.5–4.9, of *p*-xylene, 5.7–10.5, while cumene and mesitylene react still more rapidly (*Tronov*).

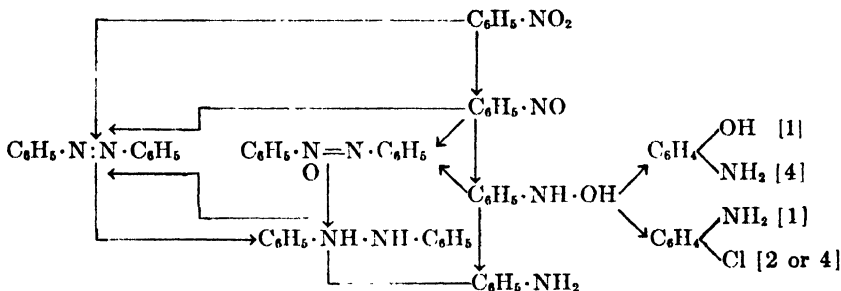
*Properties and reactions.*—The nitro-derivatives of hydrocarbons are only slightly soluble in water, but they dissolve in conc.  $\text{HNO}_3$ , and are precipitated from this solution by the addition of water. They dissolve readily in alcohol, ether, glacial acetic acid, etc. The nitro-compounds melt at rather a higher temperature than the corresponding bromo-derivatives.

A distinguishing feature of the nitro-compounds, including the nitro-phenols (p. 199) is their capacity of forming addition compounds with many aromatic and unsaturated substances. The molecular proportion, in many cases, is 1:1, and the compounds are useful for characterising the second component. The theory of the structure of these molecular compounds has been discussed by *Pfeiffer*, Ann. 412, 265 and *Organische Molekülverbindungen*, Stuttgart, 1927, and *Hertel*,

The ease of reduction of nitro-compounds is particularly important. Nitroso-compounds and  $\beta$ -phenylhydroxylamines are formed (p. 68) as primary products. If the reduction is carried out in alkaline medium, azoxy-compounds are formed and these undergo a further reduction to azo- and hydrazo-compounds. These reactions are shown in the following scheme:



The course of the electrochemical reduction, as given by *Haber* (Angew. Chem. 13, 435) is as follows:



The ease with which the nitro-compounds are reduced to substances of wide and varied application in the dyestuff industry and elsewhere, makes them important, and, indeed, indispensable as intermediates.

Hydrogen chloride at 200–300° replaces the nitro-groups of some polynitrohydrocarbons by chlorine, with further chlorination in some cases (*Lobry de Bruyn* Rec. 15, 84);  $\text{SOCl}_2$  acting at 160°, has the same effect (*Ger. Pat.* 280,739). Hydrogen in the *o*-position to  $\text{NO}_2$  is sometimes replaced by Cl when the substance is reduced with stannous chloride and hydrochloric acid (*Blanksma*). Diphenyl derivatives are formed when  $\text{AlCl}_3$  acts on nitro-derivatives of hydrocarbons dissolved in benzene homologues; nitrobenzene and toluene thus give nitrophenyltolyl (*Kliegl*, Ber. 53, 1646).

The aromatic nitro-group as such, unless it is attacked by inorganic reducing agents, behaves, as a rule, as an inert group, and because the nitrogen is at its

maximum valency, there is no addition or condensation at the nitrogen atom. Polynitro-compounds, however, form addition compounds with NaOH and NaO-Et which are often highly coloured. The structure of these compounds, in which the whole of the ring is involved, is discussed in "Organic Chemistry of Nitrogen," Oxford, 1937, p. 259. For the action of sodium on aromatic nitro-compounds, see *Lukashevitch*, Ann. 521, 198.

The ease of reduction of the nitro-group implies that it can behave as an oxidising agent, and this behaviour is shown in certain reactions, such as with Grignard compounds, and in Skraup's synthesis of quinoline. This oxidising power is very striking in certain cases of intramolecular oxidation and reduction in which a group ortho to a nitro-group is oxidised. Such oxidation often takes place during a reaction in which the group ortho to a nitro-group is involved. Then, as *Baeyer* puts it, "the nitro-group attacks the side chain at the moment of reaction" by transferring one or both of its oxygen atoms to the side chain, completing diverting the normal course of the reaction. The following examples may be mentioned: the transformation of *o*-nitrotoluene into *o*-nitrosobenzyl alcohol, anthranil into anthranilic acid (p. 63); the isomeric change of *o*-nitrophenyl propiolic ester into isotogenic ester (p. 480); the formation of indigo from *o*-nitrophenyl-hydracrylic ketone, and from *o*-nitrobenzaldehyde, acetone, and alkali (p. 276); *o*-nitrobenzaldehyde, under the influence of light, or in the presence of ammonium cyanide, isomerises to *o*-nitroso-benzoic acid (p. 276); *o*-nitrophenyl-ethylene oxide isomerises to *o*-nitroso-benzoyl-carbinol (p. 400), and *o*-nitrodiazo-acetophenone can be converted into N-hydroxy-isatin (p. 464); the last two reactions are brought about by dilute acids.

With *o*-nitro-compounds having a side-chain with an amino-group, ring closure with elimination of water from the nitro- and amino-groups sometimes takes place; see p. 103.

**NITROBENZENES.** The melting and boiling points of the nitrobenzenes which are known are shown in the following table:

| Name and formula                                       | M.p.     | B.p.           | $\mu$ |
|--------------------------------------------------------|----------|----------------|-------|
| Nitrobenzene $C_6H_5NO_2$                              | +5.82°   | 209°           | 4.03  |
| 1,2-( <i>o</i> -)Dinitrobenzene                        | 118°     | 319° (773 mm.) | 6.0   |
| 1,3-( <i>m</i> -)Dinitrobenzene } $C_6H_4(NO_2)_2$     | 91°      | 303° (771 mm.) | 3.8   |
| 1,4-( <i>p</i> -)Dinitrobenzene                        | 172°     | 299° (777 mm.) | 0.0   |
| 1,2,3-( <i>v</i> -)Trinitrobenzene                     | 127.5°   | ..             | ..    |
| 1,2,4-( <i>as</i> -)Trinitrobenzene } $C_6H_3(NO_2)_3$ | 61°      | ..             | ..    |
| 1,3,5-( <i>s</i> -)Trinitrobenzene                     | 123°     | ..             | 0.0   |
| 1,2,3,5-Tetranitrobenzene $C_6H_2(NO_2)_4$             | 125-126° | ..             | ..    |

**Nitrobenzene**,  $C_6H_5NO_2$ , was discovered in 1834 by *Mitscherlich* (Pogg. Ann. 31, 625), when he allowed benzene to react with nitric acid. It is also formed during the oxidation of aniline (p. 76). It is prepared in large quantities industrially, and is used for the manufacture of aniline. In the industrial preparation of nitrobenzene a mixture of nitric and sulphuric acids is allowed to flow into benzene in cast-iron vessels and kept stirred. Nitrobenzene is a yellowish, highly refracting liquid, density 1.20 at 20°, smelling of benzaldehyde or oil of bitter almonds, and with a sweet taste in dilute aqueous solution (*Wohl*, Ber. 27, 1817). It acts as a poison, especially when its vapour is breathed. In addition to its use in the dyeing industry, nitrobenzene is employed in the perfume industry in the perfuming of soap (artificial almond oil, oil of mirbane). In the laboratory it is often used as a solvent. Its reduction has been discussed on page 59, the most important industrial reduction product being aniline

(p. 75). Boiling with sodium sulphite reduces it to *p*-aminophenolsulphonic acid (*Seyewitz*, C.r. 174, 296). It is used as an oxidising agent in several important reactions, in both alkaline and acidic solutions (see rosaniline, quinoline). Because of its exceptionally high Kerr constant it has been used in television.

**DINITROBENZENES**,  $C_6H_4(NO_2)_2$ . When benzene is heated for some time with fuming nitric acid, or for a short time with nitric and sulphuric acids, *m*-dinitrobenzene is formed, together with a very little *o*- and *p*-dinitrobenzenes. The latter are more soluble in alcohol than the meta-compound. The meta-compound is used in the dye industry for preparing *m*-phenylene diamine.

*p*-Dinitrobenzene can be obtained from *p*-quinone dioxime (*q.v.*), and from *p*-nitroso-nitrobenzene by oxidation, and from *p*-nitrophenyl-diazonium nitrate by Sandmeyer's reaction. *o*-Dinitrobenzene can be isolated from the residue of the preparation of *m*-dinitrobenzene by dissolving it in two parts by weight of boiling nitric acid, and pouring into 5-6 parts by volume of cold nitric acid; *o*-dinitrobenzene then crystallises out (*Lobry de Bruyn*, Ber. 26, 266). The connection between temperature of nitration and yield of the three isomerides has been studied by *Wylter*, Helv. 15, 23.

The dinitrobenzenes can be partly reduced to nitranilines (p. 102) which link the phenylene diamines to the dibromobenzenes and benzene dicarboxylic or phthalic acids.

*o*-Dinitrobenzene crystallises in plates. On boiling with NaOH it gives *o*-nitrophenol, and on heating with alcoholic ammonia, *o*-nitraniline. Other aromatic *o*-dinitro compounds behave similarly.

*m*-Dinitrobenzene gives  $\alpha$ - or 2,4-dinitro-, and  $\beta$ - or 2,6-dinitro-phenol on heating with potassium ferricyanide and sodium hydroxide, or with powdered caustic potash. When treated with alcoholic KCN one nitro-group is replaced by ethoxyl, and one cyanogen group becomes attached to the ring, 2-nitro-6-ethoxy-benzonitrile being formed (*Lobry de Bruyn*, Rec. 2, 205). The last two reactions are examples of the attack of anionoid reagents (p. 22). Alkali sulphite simultaneously reduces and sulphonates, and gives *m*-nitraniline-*p*-sulphonic acid (*Nietzki*, Ber. 29, 2448).

*p*-Dinitrobenzene forms colourless needles.

When chlorine and bromine react with the dinitrobenzenes at 200°, the nitro-groups are partly or completely replaced by halogen (*Lobry de Bruyn*, Ber. 24, 3749). Sodium methylate or ethylate on warming replace one nitro-group by a methoxy- or ethoxy-group.

**TRINITROBENZENES**. 1,3,5- or *sym*-Trinitrobenzene forms snow-white leaflets; the labile form melts at 61°, and the stable form at 122° (*Rudcliffe*, Chem. and Ind. 40, 45; cry-tal structure, *Hertel*, Z. physikal. Chem. B 11, 77; electric moment, *ibid.* 27, 11). It is prepared from *m*-dinitrobenzene, or by heating trinitrobenzoic acid, or synthetically from the sodium compound of nitromalonic aldehyde by acidifying (*Hill*, Am. Chem. J. 22, 89). It can be oxidised to picric acid (2,4,6-trinitrophenol). It combines with many aromatic hydrocarbons, phenolic ethers, phenol-carboxylic esters, inorganic and organic bases to form stable addition products; similar compounds can be obtained from *m*- and *p*-dinitrobenzene, trinitrotoluene, etc. (*Sudborough*, J. 99, 209; 109, 1339, 1349; *Taylor*, Am. 44, 104). *sym*-Trinitrobenzene gives an orange colour with aqueous alkalis, possibly due to the formation of unstable salts. It also unites with sodium alkoxides to give salt-like compounds which are decomposed by water. These salts have been referred to on p. 201. When *sym*-trinitrobenzene is heated with sodium alkoxide solution one of its nitro-groups is replaced by alkoxyl (*Lobry de Bruyn*, Rec. 20, 107).

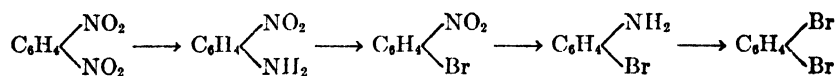
1,2,4- or *as*-Trinitrobenzene is obtained by heating *p*-dinitrobenzene with nitric and fuming sulphuric acids at 180°, or by the action of nitric acid on 2,4-dinitraniline (*Körner*, Atti R. Accad. Lincei 23, I, 633).

1,2,3- or *v*-Trinitrobenzene, m.p. 127.5°, is obtained from 2,6-dinitraniline by replacing NH<sub>2</sub> by NO<sub>2</sub> (Körner, Atti. R. Accad. Lincei 23, II, 464).

1,2,3,5- or *as*-Tetranitrobenzene, crystallises in yellow needles, m.p. 125–126°, and is obtained by dissolving picryl-hydroxylamine (Borsche, Ber. 56, 1943) or picramide (Holleman, Rec. 49, 112; Jois, J. Mysore 4, 239) in nitric acid and passing oxides of nitrogen through the solution.

**NITRO-HALOGENO-BENZENES.** Methods of formation: 1. By nitration of F-, Cl-, Br-, and I-benzenes, when chiefly *p*-, and some *o*-mononitro-halogenobenzenes are formed. 2. By treatment of nitrobenzenes with bromine or chlorine; in polynitro-compounds, a nitro-group is often replaced by halogen. 3. By reduction of dinitrobenzenes to the corresponding nitranilines, and replacing the amino-group of these by halogen by the diazo-compound and Sandmeyer's reaction. 4. By acting upon nitrophenols with PCl<sub>5</sub>, when chloro-nitro-benzenes are formed.

The halogeno-nitro-benzenes link the dinitro-, nitramino-, and diamino-benzenes to the halogen-amino- and dihalogeno-benzenes, and therefore enable the inter-relationship of these disubstitution products of benzene to be determined:



A nitro-group in the ortho- or para-position to a halogen atom makes the latter reactive, as in an alkyl halide (Vol. I, p. 162), while a nitro-group in the meta-position does not have this effect. See Lapworth, Proc. 1903, 23; Borsche, Ber. 49, 2222; 50, 1339; Hückel, Ber. 62, 2041; a synopsis is given in Hückel, Theor. Grundlagen, II, 256. A striking example of this rule is afforded by the behaviour of 1,2,4,6-tetrachloro-3,5-dinitrobenzene, in which the chlorine atoms 2, 4, and 6 can be replaced by NH<sub>2</sub>, NHPh, OEt, etc., but the Cl atom 1 in the *m*-position to both nitro-groups cannot (Jackson, Am. Chem. J. 31, 360). The more nitro-groups which are suitably placed in the ring, the more reactive is the halogen atom; 2,4,6-trinitro-chlorobenzene (picryl chloride) behaves like an acid chloride (Borsche, Ber. 46, 2117). In some cases a nitro-group, and not the halogen, is lost; cf. dinitro-chloro- and 3,4,6-trinitro-chlorobenzenes.

| Compound                                           | 1,2-  | 1,3-                         | 1,4-   |
|----------------------------------------------------|-------|------------------------------|--------|
| C <sub>6</sub> H <sub>4</sub> F(NO <sub>2</sub> )  | −5.9° | +4.1° and +3.1° (dimorphous) | +26.5° |
| C <sub>6</sub> H <sub>4</sub> Cl(NO <sub>2</sub> ) | 32.5° | 44° and 24°                  | 83.5°  |
| C <sub>6</sub> H <sub>4</sub> Br(NO <sub>2</sub> ) | 43.1° | 56° and 17.4°                | 127°   |
| C <sub>6</sub> H <sub>4</sub> I(NO <sub>2</sub> )  | 52°   | 36° and 9.9°                 | 174°   |

The melting points of the isomeric monofluoro-, monochloro-, monobromo-, and monoiodo-nitrobenzenes are given in the table above (Steinmetz, Z. Krist. 54, 467).

In *p*-fluoro-nitrobenzene the F-atom is very reactive, and is readily replaced by alkoxy, for example (Rarick, Am. 55, 1289). The *m*-halogeno-nitrobenzenes all occur in a stable high-melting and an unstable low-melting form (Hasselblatt, Z. physikal. Chem. A 83, 12). The electric moments of the chloronitro-benzenes are *o*-, 4.3, *m*-3.4, *p*-2.5<sub>6</sub> D.

Among the many nitro-halogeno-benzenes which are known, 3,4-dinitrochlorobenzene should be mentioned. It has been obtained in four crystalline modifications, melting at 28°, 36°, 37.1°, and 40.5°, and a liquid modification also exists (Holleman, Rec. 35, 48).

3,5-Dinitrochlorobenzene, m.p. 65.4°, is obtained by chlorinating *m*-dinitrobenzene. When it is heated with sodium ethoxide in EtOH, it exchanges not the Cl atom, but a NO<sub>2</sub>-group for OEt, and forms a nitrochloro-phenol ether (Lobry de Bruyn, Rec. 20, 107).

3,4,6-Trinitrochlorobenzene, m.p. 116°, obtained by further nitration of 1-chloro-3,4-dinitrobenzene, behaves similarly. By the action of ammonia, NO<sub>2</sub> in the 3-position is replaced by NH<sub>2</sub> (Nietzki, Ber. 36, 3953).

**1,2-Dichloro-4,5-dinitrobenzene**, m.p. 114°, and **1,2-dichloro-3,4-dinitrobenzene**, m.p. 97°, are produced together when *o*-dichlorobenzene is nitrated. When heated with ammonia, the first exchanges a nitro-group, and the second a Cl-atom for NH<sub>2</sub> (*Nietzki*, Ber. **37**, 3892). Other dinitro-dichloro-benzenes have been described by *Holleman*, Rec. **39**, 435.

**2,4,6-Trinitrochlorobenzene, picryl chloride**, C<sub>6</sub>H<sub>2</sub>Cl(NO<sub>2</sub>)<sub>3</sub>, m.p. 83°, is obtained from picric acid by the action of PCl<sub>5</sub>. With aqueous ammonia it gives **picramide**, C<sub>6</sub>H<sub>2</sub>(NH<sub>2</sub>)(NO<sub>2</sub>)<sub>3</sub>, m.p. 190°, and when boiled with sodium carbonate picric acid is regenerated. **Picryl bromide**, C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>Br, m.p. 123°, is obtained from bromo-dinitrobenzene by the action of nitric acid (*Jackson*, Am. Chem. J. **29**, 216). For the addition products formed from picramide and hydrocarbons and for the isomeric trinitro-chlorobenzenes, see *Holleman*, Rec. **40**, 67; *Trans. Amsterdam* **31**, 294; cf. *Jefremov*, C., 1923, III, 380. **Dichlorodinitrobenzenes** and their transformation products are described by *Blanksma*, Rec. **21**, 269, 286, 419, 424, and **trichlorodinitrobenzene** by *Jackson*, Am. Chem. J. **18**, 664.

Of the six isomeric **dibromonitrobenzenes** five can be obtained by direct nitration of the three dibromobenzenes:

- o*-Dibromobenzene gives (a) **1,2-dibromo-4-nitrobenzene**, m.p. 58°, chief product  
(b) **1,2-dibromo-3-nitrobenzene**, m.p. 85.2°, by-product
- m*-Dibromobenzene gives (a) **1,3-dibromo-4-nitrobenzene**, m.p. 62°, chief product  
(b) **1,3-dibromo-2-nitrobenzene**, m.p. 83°, by-product
- p*-Dibromobenzene gives (a) **1,4-dibromo-2-nitrobenzene**, m.p. 84°

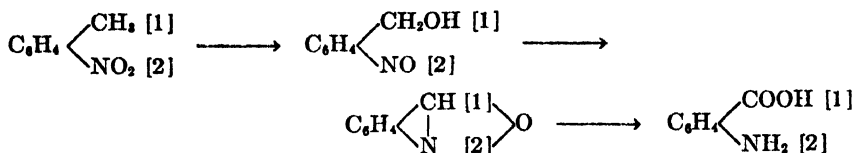
The missing **1,3-dibromo-5-nitrobenzene**, m.p. 104.5°, has been prepared by *Körner* from dibromo-*p*-nitraniline by elimination of the amino-group. For the conversion of the dibromonitrobenzenes into tribromobenzenes, see p. 11, where its importance in the determination of the constitution of benzene is discussed.

**NITROTOLUENES.** **1,2- or *o*-Nitrotoluene** exists in two forms, m.p. -9° and -4°, b.p. 222°; dipole moment 3.7 D. **1,4- or *p*-Nitrotoluene**, m.p. 51.4°, b.p. 238°, dipole moment 4.3<sub>8</sub> D. Both are obtained by nitrating toluene, and are separated by fractional distillation. The toluidines are their reduction products and are of commercial importance. When the nitration is carried out at -55°, 5.5 times as much *p*- and *o*-nitrotoluene is formed (*Pictet*, C.r. **116**, 815); at higher temperatures fuming nitric acid also produces mainly *p*-nitrotoluene, but a mixture of nitric and sulphuric acids, at low temperatures, gives about 66% of *o*-nitrotoluene. The rate of nitration under varying conditions has been determined by *Ingold*, J. **1931**, 1959.

Further nitration of *o*- and *p*-nitrotoluenes gives **2,4-dinitrotoluene**, m.p. 71°, **2,5-dinitrotoluene**, m.p. 52.5° (*Nietzki*, Ber. **21**, 433; *Rozanski*, Ber. **22**, 679), and **2,4,6-( $\alpha$ )-trinitrotoluene**, b.p. 81°. The last-named compound decomposes slowly at 150° and explodes at about 310°. Its crystal structure has been investigated by *Hertel*, Z. physik. Chem. B **11**, 77. It gives coloured molecular compounds with 1,2, or 3 mols. of NaOEt (*Giua*, Atti Torino, 1927, 62). It is an important explosive and is known industrially as *trotyl*, *tritol*, or *T.N.T.* **Isomeric trinitrotoluenes**: **2,3,4-( $\beta$ -)**, m.p. 112°; **2,4,5-( $\gamma$ -)**, m.p. 104°; **3,4,5-( $\delta$ -)**, m.p. 137.5°; **2,3,5-( $\epsilon$ -)**, m.p. 97.2°; **2,3,6-( $\eta$ -)**, m.p. 111° (*Will*, Ber. **47**, 704; *Körner*, Atti. R. Accad. Lincei **23**, 11, 464; **24**, 888; **25**, 11, 339; *Marqueyrol*, Bull. **27**, 426; *Brady*, J. **117**, 876, 1137; *Drew*, *ibid.* 1615).

The conversion of *o*-nitrotoluene into anthranilic acid when it is heated with caustic alkalis is remarkable; *o*-nitrosobenzyl alcohol and anthranil have been isolated as intermediate products (see p. 321). The successive stages in the reaction seem to be:

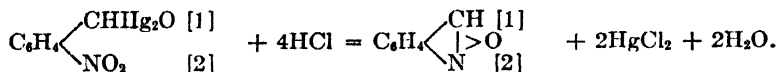




In a similar manner anthranil-sulphonic acid is obtained from *o*-nitrotoluene-sulphonic acid, and dibromoanthranilic acid is formed from *o*-nitrotoluene and bromine at 170°.

When heated with HgO in alkaline solution, *o*-nitrotoluene gives a mono- and a di-mercuric compound. The latter probably has the formula NO<sub>2</sub>[1]C<sub>6</sub>H<sub>4</sub>[2]-

CH  $\begin{array}{l} \text{Hg} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ ; it forms dark-yellow crystals which decompose on heating above 220°, and which with cold concentrated hydrochloric acid break up smoothly into mercuric chloride and anthranil (p. 278) (*Reussert*, Ber. 40, 4209; Ger. Pat. 194,364).



*o*-Nitro- and 2,4-dinitro-toluene also react with HgO.

*m*-Nitrotoluene, m.p. 16°, b.p. 230°, dipole moment 4.1<sub>3</sub> D., is formed when aceto-*p*-toluidide is nitrated, and the amino-group subsequently replaced by H. Further nitration of *m*-nitraniline gives 3,4-dinitrotoluene, m.p. 61°, and 3,5-dinitrotoluene, m.p. 93° (*Haussermann*, Ber. 27, 2209). 2,3-Dinitrotoluene, m.p. 63°. 2,6-Dinitrotoluene, m.p. 65°, when heated with bromine and magnesium carbonate in a sealed tube at 140° gives 2,6-dinitrobenzyl bromide (*Reich*, Bull. 22, 114). For the electrochemical oxidation of the isomeric dinitrotoluenes, see *Fichter*, Helv. 3, 395. 2,3,4,6-Tetranitrotoluene, m.p. 136.5°, is obtained from the 2,4,6-trinitro-compound of *m*-cresol-methyl ether, which is converted by MeOH and Ni<sub>2</sub>OH into 2,4,6-trinitro-3-aminotoluene; the latter gives tetranitrotoluene with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (*Holleman*, Rec. 49, 501).

**NITRO-DERIVATIVES OF OTHER ALKYL-BENZENES.** The ease with which aromatic nitro-compounds are formed frequently affords a means of detecting and identifying their parent hydrocarbons. Some of them are given below; for further details see *Brady*, J. 1934, 114.

| Compound                                                                                              | M.p.                 |
|-------------------------------------------------------------------------------------------------------|----------------------|
| 4-Nitro- <i>o</i> -xylene NO <sub>2</sub> [4]C <sub>6</sub> H <sub>3</sub> [1,2]Me <sub>2</sub> ..... | 29° <sup>a, b</sup>  |
| 4,5-Dinitro- <i>o</i> -xylene.....                                                                    | 116° <sup>c</sup>    |
| 4,6-Dinitro- <i>o</i> -xylene.....                                                                    | 176° <sup>c</sup>    |
| 3,4,5-Trinitro- <i>o</i> -xylene.....                                                                 | 115°                 |
| 3,4,6-Trinitro- <i>o</i> -xylene.....                                                                 | 72°                  |
| 5-Nitro- <i>m</i> -xylene.....                                                                        | 74°                  |
| 2,4-Dinitro- <i>m</i> -xylene.....                                                                    | 82°                  |
| 4,6-Dinitro- <i>m</i> -xylene.....                                                                    | 94°                  |
| 2,4,6-Trinitro- <i>m</i> -xylene.....                                                                 | 182° <sup>d</sup>    |
| 4,5,6-Trinitro- <i>m</i> -xylene.....                                                                 | 125° <sup>e, f</sup> |
| 2-Nitro- <i>p</i> -xylene, b. p. 239°.....                                                            | °                    |
| 2,6-Dinitro- <i>p</i> -xylene.....                                                                    | 123°                 |
| 2,3-Dinitro- <i>p</i> -xylene.....                                                                    | 93°                  |
| (2,6- and 2,3- double compound).....                                                                  | 99° <sup>h</sup>     |
| 2,3,5-Trinitro- <i>p</i> -xylene.....                                                                 | 139° <sup>i</sup>    |
| (one NO <sub>2</sub> replaced by OH: <i>Blanksma</i> , Rec. 24, 49).....                              |                      |

| Compound                                                                                                                       | M.p.                     |
|--------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| 2,4-Dinitro-ethyl-benzene, b.p. 163° (10 mm.)                                                                                  |                          |
| 2,4,6-Trinitro-ethyl-benzene.....                                                                                              | 37° <sup>i</sup>         |
| Nitromesitylene NO <sub>2</sub> [2]C <sub>6</sub> H <sub>2</sub> [1,3,5]Me <sub>3</sub> .....                                  | 44° <sup>k</sup>         |
| Dinitromesitylene.....                                                                                                         | 86° <sup>i</sup>         |
| Trinitromesitylene.....                                                                                                        | 232°                     |
| Nitropseudocumene NO <sub>2</sub> [5]C <sub>6</sub> H <sub>3</sub> [1,2,4]Me <sub>3</sub> .....                                | 71° <sup>k</sup>         |
| Dinitropseudocumene (NO <sub>2</sub> ) <sub>2</sub> [3,5]C <sub>6</sub> H[1,2,4]Me <sub>3</sub> .....                          | 172°                     |
| 3,5,6-Trinitropseudocumene (NO <sub>2</sub> ) <sub>2</sub> [3,5,6]C <sub>6</sub> [1,2,4]Me <sub>3</sub> .....                  | 185° <sup>m</sup>        |
| 4,5,6-Trinitro- <i>v</i> -trimethyl-benzene (NO <sub>2</sub> ) <sub>3</sub> [4,5,6]C <sub>6</sub> [1,2,3]Me <sub>3</sub> ..... | 209° <sup>n</sup>        |
| Nitro- <i>v</i> -tetramethyl-benzene NO <sub>2</sub> [5]C <sub>6</sub> H[1,2,3,4]Me <sub>4</sub> .....                         | 61° <sup>o</sup>         |
| Dinitro- <i>v</i> -tetramethyl-benzene.....                                                                                    | 178°                     |
| Dinitro-isodurene (NO <sub>2</sub> ) <sub>2</sub> [4,6]C <sub>6</sub> [1,2,3,5]Me <sub>4</sub> .....                           | 156°                     |
| Dinitro-durene (NO <sub>2</sub> ) <sub>2</sub> [3,6]C <sub>6</sub> [1,2,4,5]Me <sub>4</sub> .....                              | 205°                     |
| Nitro-pentamethyl-benzene.....                                                                                                 | 154° <sup>p</sup>        |
| 3-Nitrocymene.....                                                                                                             | 70°                      |
| 2,3-Dinitrocymene.....                                                                                                         | 154°                     |
| 2,5-Dinitrocymene.....                                                                                                         | 77- 78°                  |
| 2,6-Dinitro-cymene (from <i>p</i> -cymene + HNO <sub>3</sub> ).....                                                            |                          |
| 2,3,6-Trinitro-cymene (from 2,3- or 3,5-dinitro).....                                                                          | 124-125° <sup>r, s</sup> |
| <i>p</i> -Nitro- <i>ψ</i> -butyl-benzene, b.p. 137-138° (15 mm.).....                                                          |                          |
| Dinitro- <i>ψ</i> -butyl-benzene.....                                                                                          | 62° <sup>t</sup>         |

<sup>a</sup> Jacobsen, Ber. 17, 160. <sup>b</sup> Noelting, Ber. 18, 2670. <sup>c</sup> Noelting, Ber. 35, 628. <sup>d</sup> Grevingh, Ber. 17, 2424. <sup>e</sup> Blonskma, Rec. 25, 165. <sup>f</sup> Crossley, J. 95, 202. <sup>g</sup> Noelting, Ber. 18, 2680. <sup>h</sup> Barner, Ber. 15, 2304. <sup>i</sup> Noelting, Ber. 19, 145. <sup>j</sup> Schultz, Ber. 42, 2633. <sup>k</sup> Bamberger, Ber. 33, 3625; Powell, Johnson, Org. Syntheses, 14, 68. <sup>l</sup> Kononov, Ber. 29, 2201. <sup>m</sup> Schultz, Ber. 42, 3608. <sup>n</sup> Jacobsen, Ber. 19, 2517. <sup>o</sup> Tohl, Ber. 21, 905. <sup>p</sup> Willstätter, Ber. 42, 4162. <sup>q</sup> C. 1918, II, 951. <sup>r</sup> Ehrenrooth, C. 1932, I, 3418. <sup>s</sup> Aschan, C. 1919, I, 227; <sup>t</sup> Du Toit-Malherbe, Ber. 52, 319.

The di- and tri-nitro-derivatives of certain *ψ*-butyl-benzenes have a strong smell of musk and are used as artificial musk in the perfume industry (Baur, Ber. 24, 2832). 2,4,6-Trinitro-3-*tert*.butyl-toluene, (NO<sub>2</sub>)<sub>3</sub>[2,4,6]C<sub>6</sub>H[1]Me[3]CMe<sub>3</sub>, *toluene musk*, m.p. 97°, is reduced by SnCl<sub>2</sub> and HCl to the trihydrochloride of 2,4,6-triamino-*m*-*tert*.butyl-toluene (Herzig, Mo. 37, 567). 2,4,6-Trinitro-5-*tert*.butyl-*m*-xylene, *xylene musk* is dimorphous, the m.p. of the two forms being 105-106° and 112-113°. Dinitro-*tert*.butyl-*p*-cymene, *cymene musk*, *moskene*, m.p. 132.5°, is obtained, together with two isomers, m.p. 126° and 145°, from *p*-cymene (Barbier, Helv. 15, 592). The corresponding derivative of *m*-cymene, m.p. 155°, does not smell so strongly of musk. Similar nitro-derivatives from other benzene compounds are marketed as *aldehyde musk*, *ketone musk*, etc.

**NITROHALOGENO-DERIVATIVES OF ALKYL BENZENES.** A large number of these compounds have been prepared.

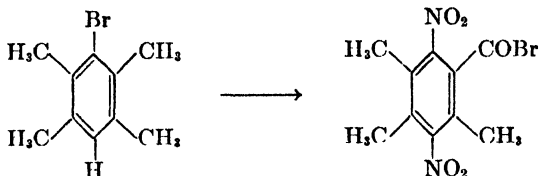
4-Fluoro-3-nitrotoluene, m.p. 27°, is obtained, together with *m*-nitrocresol, by nitrating *p*-fluorotoluene (Le Blanc, Z. Elektrochem. 20, 543).

2-Chloro-5-nitrotoluene, m.p. 44°, and 4-chloro-2-nitrotoluene, m.p. 38°, are the nitration products of *o*- and *p*-chlorotoluene, respectively. 3-Chloro-4-nitrotoluene, m.p. 55° has been obtained from nitro-*m*-toluidine. For other halogeno-nitrotoluenes see Noelting, Ber. 37, 1018; Wibaut, Rec. 32, 244; Morgan, J. 117, 784.

2,4,6-Trinitro-5-chlorotoluene, m.p. 148°, is formed, together with the 2,4-dinitro-compound when *m*-chlorotoluene is nitrated. It is a homologue of picryl chloride, and its chlorine atom is similarly reactive and readily exchanged for many other groups (Reverdin, Ber. 37, 2093).

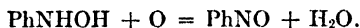
Nitrobromodurene, m.p. 178°, has been prepared by Willstätter, (Ber. 42, 4157) by nitrating bromodurene in chloroform with nitro-sulphuric acid. Fuming

nitric acid has a very curious action on bromodurene; the bromine atom migrates, oxidation occurs, and dinitro-durylic bromide is produced:

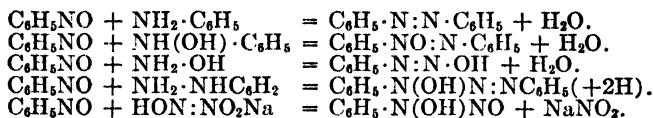


### (b) Nitroso-derivatives of Benzene and Alkyl-benzenes

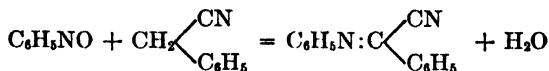
The mononitroso-derivatives of benzene hydrocarbons cannot be obtained by direct substitution of the hydrocarbon. They are formed: 1. By oxidising  $\beta$ -hydroxylamine derivatives (p. 68) with potassium dichromate and sulphuric acid, ferric chloride, or air:



2. By oxidising anilines with permounsulphuric acid (*Bamberger*, Ber. 32, 1675). 3. By electrolytic reduction of nitrobenzene without a diaphragm in a neutral electrolyte, such as a solution of sodium, magnesium, or aluminium sulphate. Small amounts are formed when the vapours of nitro-compounds are passed over iron powder at  $220^\circ$  in a current of  $\text{CO}_2$  (*Rinker*, Weekbl. 11, 1062). The electrochemical formation seems to be a secondary process, the  $\beta$ -phenylhydroxylamine first formed at the cathode being oxidised to nitrobenzene at the anode (Ger. Pat. 192,519). In the solid state the simple aromatic nitroso-compounds form colourless volatile crystals, but in the liquid state and in solution they are green. The reason for this change of colour is dissociation; in the solid state the compounds exist as double molecules, which break down to single molecules in the liquid state (*Bamberger*, Ber. 34, 3877). The dimeric molecules are possibly held together by a N—N linking similar to that in azoxy-compounds. In a 1% benzene solution nitroso benzene itself is not appreciably associated, but substitution, especially in the ortho-position relative to NO, increases association. The percentage of associated molecules in a 1% benzene solution is 9.2 for *o*-nitrosotoluene 11.3 for nitrosomesitylene, and 30.9% for 2,4,6-tribromonitrosobenzene (*Hammick*, J. 1931, 3105; 1934, 29). On oxidation, the nitrosobenzenes give nitro-compounds, and on reduction, amino-compounds. They condense with aromatic amines to give azo-compounds, water being eliminated; with  $\beta$ -phenylhydroxylamine to give azoxy-compounds; with hydroxylamine to give the isodiazobenzenes; with phenylhydrazines to give diazo-hydroxyamino-compounds; and with the salts of nitro-hydroxylamic acid (Vol. I, 206), or benzene sulphohydroxamic acid, to form  $\beta$ -phenyl-nitroso-hydroxylamines (*Bamberger*, Ber. 28, 245, 1218; 29, 102; 32, 3554; *Angeli*, Gazz. 33, II, 239).



With substances containing reactive  $\text{CH}_2$ -groups the nitrosobenzenes give keto-anils with loss of water, e.g.,



(*Sachs*, Ber. 34, 494). Conc. sulphuric acid causes them to polymerise to compounds resembling aldols, e.g., *p*-nitroso-diphenyl-hydroxylamines,  $\text{NO} \cdot \text{C}_6\text{H}_4\text{N}(\text{OH})\text{Ph}$  (*Bamberger*, Ber. 31, 1513; 32, 219; cf. p. 70). In these reactions nitro-

sobenzene shows a striking resemblance to aldehydes, especially benzaldehyde,  $\text{PhCHO}$  (p. 298) from which it differs by a N-atom taking the place of CH. With diazomethane (Vol. I, p. 251) the nitrosobenzenes give addition products which tend to lose nitrogen and go over into glyoxime phenyl ethers (p. 100) (*Pechmann*, Ber. 30, 2791). Catalytic reduction with  $\text{PtO}_2$  produces amines directly, with no intermediate formation of hydroxylamine derivatives (*Cusmano*, Atti. R. Accad. Lincei 26, II, 87). The nitrosobenzenes react with anilines to give azo-compounds (*Ritter*, Am. 52, 1815). With Grignard reagents diaryl-hydroxylamines are formed (*Wreland*, Ber. 48, 1117). For the action of Na on the nitroso-compounds see *Lukaschewitsch*, Ann. 521, 198.

**Nitrosobenzene**,  $\text{C}_6\text{H}_5\text{NO}$ , m.p.  $68^\circ$ , was first obtained in solution by the action of nitrosyl bromide on  $\text{HgPh}_2$  (*Baeyer*, 1874); cf. the action of NO on  $\text{HgPh}_2$  (*Bamberger*, Ber. 30, 506; 31, 1528), and that of NOCl on  $\text{PhMgBr}$  (*Oddo*, Gazz. 39, I, 659). It is prepared by oxidising  $\beta$ -phenylhydroxylamine or aniline, or by the electrolytic reduction of nitrobenzene. Small amounts are produced, in addition to other products, when phenyldiazonium chloride is oxidised, and when azoxybenzene is distilled. It is completely destroyed when exposed to light, azoxybenzene, nitrobenzene, aniline, and *o*-hydroxy-azobenzene, with some resinous matter being formed (*Bamberger*, Ber. 27, 1182, 1273; 35, 1606).

Direct introduction of other substituents into nitrosobenzene cannot be effected.

*o*-, *m*-, and *p*-**Nitrosotoluenes**,  $\text{C}_6\text{H}_4\cdot\text{CH}_3\cdot\text{NO}$ , m.p.  $72^\circ$ ,  $53^\circ$ , and  $48^\circ$ , respectively. 2,3-, 2,4-, 2,5-, 2,6-, and 3,4-**Nitrosoxylenes**,  $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NO}$ , m.p.  $91^\circ$ ,  $41^\circ$ ,  $101^\circ$ ,  $141^\circ$  (decomp.),  $45^\circ$ , respectively. **Nitrosomesitylene**,  $\text{Me}_3\cdot\text{C}_6\text{H}_2\cdot\text{NO}$ , m.p.  $122^\circ$ , is best prepared from amino-mesitylene (mesidine) by the action of permonosulphuric acid (*Bamberger*, Ann. 316, 275). *p*-**Chloro-** and *p*-**bromonitrosobenzenes**, m.p.  $87^\circ$  and  $92^\circ$ , respectively.

*o*-, *m*-, and *p*-**Nitro-nitrosobenzenes**, m.p.  $126^\circ$ ,  $90^\circ$ ,  $119^\circ$ , respectively, are obtained by oxidising the three nitranilines with permonosulphuric acid (*Bamberger*, Ber. 36, 3803; *Brand*, Ber. 38, 4011). The *o*- and *p*-compounds are also obtained by reducing *o*- and *p*-dinitrobenzene with hydroxylamine or SnO in strongly alkaline MeOH solution. The first products of this reaction are highly

coloured alkali salts of a dinitronic acid with a quinone structure,  $\text{C}_6\text{H}_4\begin{matrix} \text{NOOK} \\ \diagdown \\ \text{NOOK} \end{matrix}$ ,

which when acidified lose water and give nitro-nitrosobenzenes. By similar methods the following can be obtained: *o*-**nitroso-*p*-xylene**, m.p.  $130.5^\circ$ , from *o*-dinitro-*p*-xylene; 3-**nitro-4-nitroso-** and 4-**nitro-3-nitroso-toluenes**, m.p.  $143^\circ$  and  $141^\circ$ , from 3,4-dinitrotoluene; 2-**nitro-3-nitroso-** and 3-**nitro-2-nitrosotoluenes**, m.p.  $92-93^\circ$  and  $126-127^\circ$ . *m*-Dinitrobenzene is not reduced under these conditions but forms dinitro-amino-compounds, by substitution (*Meisenheimer*, Ber. 39, 2526, 2533; 52, 1161). **Trinitro-nitroso-benzene**,  $(\text{NO}_2)_3[2,4,6]\text{C}_6\text{H}_2\text{NO}$ , m.p.  $198^\circ$  (*Nietzki*, Ber. 34, 59). 2-**Nitro-6-nitrosotoluene**, m.p.  $117^\circ$ ; 2-**nitro-4-nitrosotoluene**, m.p.  $87^\circ$  (*Brand*, Ber. 40, 3331).

Certain compounds, formerly believed to be *o*-dinitroso-compounds, are obtained from *o*-nitro-phenyl azide (*Zincke*, Ann. 307, 28), or, more readily, by the action of hypochlorite on *o*-nitranilines (*Green*, *Rowe*, J. 101, 2443, 2452). They

are actually benzo-furoxanes,  $\text{C}_6\text{H}_4\begin{matrix} \text{NO} \\ \diagdown \\ \text{N} \end{matrix}\text{O}$ , as was shown by *Hammick* (J. 1931, 3308).

*p*-**Dinitroso-**derivatives are formed in the oxidation of *p*-quinone dioximes with potassium ferricyanide in alkaline solution.

*p*-**Dinitrosotoluene**,  $\text{Me}\cdot\text{C}_6\text{H}_4(\text{NO})_2$ , m.p.  $133^\circ$ , is obtained from toluquinone dioxime. It forms yellow needles with the characteristic sharp smell of quinone. It is converted into *p*-dinitrotoluene by fuming nitric acid, and into toluquinone dioxime by hydroxylamine hydrochloride (*Melene*, Ber. 21, 734; *Kehrmann*, Ber. 21, 3319). *m*-**Dinitrosobenzene**,  $\text{C}_6\text{H}_4(\text{NO})_2$ , m.p.  $146.5^\circ$ , is formed, together with *m*-nitro-nitrosobenzene, in the reduction of *m*-dinitrobenzene with zinc dust and acetic acid in alcoholic solution (*Alway*, Ber. 38, 1899).

1,2,3,4-**Tetranitrosobenzene**,  $\text{C}_6\text{H}_2(\text{NO})_4$ , m.p.  $93^\circ$ , is obtained from diquinoyl-tetroxime by the action of sodium hypochlorite. 1,2-3,5-**Dinitro-dinitroso-**

benzene,  $C_6H_2(NO_2)_2(NO)_2$ , m.p.  $133^\circ$ , golden leaflets, is obtained from picryl chloride (p. 63) by the action of hydroxylamine in acetic acid solution; on oxidation it gives *as*-tetranitrobenzene (*Nietzke*, Ber. 32, 505; 34, 55).

In *o*- and *p*-bromo-nitroso-benzene the bromine atoms are as loosely bound as in the corresponding bromo-nitro-benzenes (*Hammick*, J. 1932, 742). M.p., *o*-,  $98^\circ$ , *m*-,  $78^\circ$ , *p*-,  $92^\circ$ .

Compounds of the general formula  $R \cdot N(O) : CR^1R^2$ , produced by the action of aliphatic or aromatic-aliphatic diazo-compounds  $R^1R^2CN_2$  on nitroso-compounds, are called *nitrones*. They are the N-ethers of oximes of aldehydes or ketones, and in some cases can be obtained by the action of N-substituted hydroxylamines on aldehydes and ketones. They have been called nitrones by *Staudinger* (Ber. 22, 720). Diphenyl-N-phenyl-nitron, m.p.  $216-217^\circ$  (decomp.) has been obtained by *Staudinger* (Helv. 2, 534) from diphenyl-diazomethane and nitroso-benzene in benzene solution.

### (c) N-Aryl-hydroxylamines\*

These very reactive substances are intermediate products in the reduction of nitro- and nitroso-benzenes. They are very sensitive to alkalis and acids, and are best prepared with neutral reducing agents, such as zinc dust in  $NH_4Cl$  solution, or  $NaSH$  (*Lapworth*, J. 119, 765; *Wislicenus*, Ber. 29, 494; *Bamberger*, Ber. 29, 863; *Goldschmidt*, Ber. 29, 2307; *Brand*, Ber. 38, 3076), with the nitrobenzenes, or Al-amalgam and water acting upon an ethereal solution of a nitrobenzene (*Marvel*, Am. 41, 276). They are formed very smoothly by electrolytic reduction of nitro-compounds in an acetic acid-sodium acetate solution (*Brand*, loc. cit.), or in a solution which is kept neutral or feebly acidic by addition of acids, acid salts, or buffers (Ger. Pat. 488,947). They can also be prepared with alcoholic ammonium sulphides, polynitro-compounds being partially reduced by this reagent to nitro-aryl-hydroxylamines (*Willstätter*, Ber. 41, 1936). Nitrophenol ethers, such as 2,4-dinitro-anisole, exchange their alkoxyl groups when treated with hydroxylamine hydrochloride and sodium hypochlorite, and give nitro-N-phenyl-hydroxylamines (*Borsche*, Ber. 56, 1494). *Bamberger* (Ber. 32, 1675) obtained N-phenyl-hydroxylamine by oxidising aniline with permonosulphuric acid.

The aryl-hydroxylamines reduce ammoniacal silver nitrate and Fehling's solution. Their aqueous solutions rapidly absorb oxygen from the air, especially in the presence of alkali, hydrogen peroxide being formed. The primary oxidation products are nitrosobenzenes (p. 66), which, however, usually combine with unchanged aryl-hydroxylamine to form azoxy-benzenes:



Methyl groups in the *o*- or *p*-position retard this reaction so that in mesityl-hydroxylamine it does not occur at all (*Bamberger*, Ann. 316, 257).

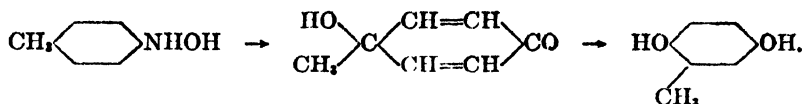
With diazonium solutions, the aryl-hydroxylamines give diazo-hydroxyamino-compounds, e.g.,  $PhN(OH)N_2Ph$ ; this reaction is also hindered by *o*- and *p*-methyl groups.

Phenyl-hydroxylamine, and other hydroxylamines in which the *p*-position is free are converted into *p*-aminophenols by dilute sulphuric acid:



When the *p*-position is occupied by a methyl group, the rearrangement still takes place, but  $NH_2$  is eliminated, and the so-called "quinols" are formed; these are related to the quinones (p. 233) and undergo a further isomeric change to hydroquinones:

\* There are two possible types of substitution products of hydroxylamine,  $R \cdot NHOH$ , and  $NH_2OR$ . These were formerly called the  $\beta$ - and the  $\alpha$ -derivatives. It is, however, better to call them the N- and O-derivatives, the prefixes being more explicit.



Concentrated sulphuric acid converts phenyl-hydroxylamine into *p*-amino-phenol-*o*-sulphonic acid. Conc. HCl converts *m*-tolyl-hydroxylamine into chlorotoluidines (*Bamberger*, Ber. 33, 3600; 34, 61; 35, 3697). These reactions recall the conversion of aromatic nitramines, nitrosoamines, and chloramines into *p*-nitro, *p*-nitroso-, and chloro-anilines, respectively. For a discussion of their mechanism see "Organic Chemistry of Nitrogen," Oxford, 1937, p. 163.

With aldehydes, such as benzaldehyde, the aryl-hydroxylamines give N-ethers of the oximes (nitrones), e.g.,  $\text{PhN}=\text{CHPh}$ , water being eliminated (*Plancher*,

Atti. Accad. Lincei 14, II, 36), but formaldehyde gives *methylenc-diaryl-hydroxylamines*, e.g.,  $\text{CH}_2[\text{N}(\text{OH})\text{Ph}]_2$ . This compound changes readily into glyoxime N-phenyl-ether (p. 100), while anhydrous  $\text{CuSO}_4$  converts it into diphenyl-hydroxyformamidine,  $\text{CH} \begin{array}{l} \text{N}(\text{OH})\text{Ph} \\ \text{NPh} \end{array}$  (p. 90).

Acid chlorides give the N-acyl-derivatives of the aryl-hydroxylamines forming, e.g., N-formyl-phenylhydroxylamine,  $\text{PhN}(\text{CHO})\text{OH}$ , m.p. 71°, N-acetyl-phenylhydroxylamine,  $\text{PhN}(\text{Ac})\text{OH}$ , m.p. 67°, N-benzenesulphonyl-phenylhydroxylamine,  $\text{PhN}(\text{SO}_2\text{Ph})\text{OH}$  (*Bamberger*, Ber. 34, 243; 35, 1883).

N-Phenylhydroxylamine,  $\text{C}_6\text{H}_5\text{NHOH}$ , m.p. 82°, forms a hydrochloride which is precipitated from ether in white crystalline flakes, and also forms metallic salts, e.g., with sodium in ether:  $\text{PhNHONa}$ .

In addition to the reactions mentioned above the formation of nitroso-phenylhydroxylamine (see below) with  $\text{N}_2\text{O}_5$ , and the formation of *phenyl-sulphamic acid*,  $\text{PhNHSO}_3\text{H}$ , with  $\text{SO}_2$  in ether, should be mentioned; in aqueous solution with  $\text{SO}_2$  phenylhydroxylamine gives *o*-aniline-sulphonic acid (*Bamberger*, Ber. 34, 246). With 1,3-dinitro- or 1,3,5-trinitro-benzene, in alkaline solution, it gives the two possible isomeric forms of 3-nitro- or 3,5-dinitro-azoxybenzene,  $\text{PhN}(\text{O})\text{:NC}_6\text{H}_4\text{NO}_2$  and  $\text{PhN}(\text{O})\text{:N}(\text{O})\text{C}_6\text{H}_3(\text{NO}_2)_2$  or  $\text{---C}_6\text{H}_3(\text{NO}_2)_2$  (*Meisenheimer*, Ber. 53, 358). Condensation products with hydroxymethylene compounds have been prepared by *Rupe* (Helv. 5, 205, 217).

O-Ethers of unsubstituted phenylhydroxylamine are unknown, but O-ethers of N-benzoyl- and N-carboxethyl-phenylhydroxylamine have been prepared. *Bamberger* believed that a substance obtained by him from the base by the action of dimethyl sulphate might be the N-methyl-ether (Ber. 52, 1093). He also studied the action of dilute sulphuric acid on phenyl- and tolyl-hydroxylamines (Ann. 390, 131). For the action of cyanogen bromide see *Wieland*, Ber. 37, 1536. For the thermal decomposition of phenylhydroxylamine to azobenzene see *Müller*, Angew. Chem. 46, 691.

*o*-, *m*-, *p*-Tolylhydroxylamine,  $\text{CH}_3\text{C}_6\text{H}_4\text{NHOH}$ , m.p. 44°, 68°, 94°, respectively; 2,3-, 2,4-, 2,5-, 2,6-, and 3,4-xylylhydroxylamine,  $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NHOH}$ , m.p. 74°, 64°, 91°, 98°, and 101°, respectively. Mesityl-hydroxylamine,  $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{NHOH}$ , m.p. 116°.

*p*-Chloro-phenylhydroxylamine,  $\text{ClC}_6\text{H}_4\text{NHOH}$ , m.p. 88°; *m*-nitrophenylhydroxylamine,  $\text{NO}_2\text{C}_6\text{H}_4\text{NHOH}$ , m.p. 119°, is obtained by electrolytic reduction of *m*-dinitrobenzene (*Brand*, Ber. 38, 3078). 2,4-Dinitro-phenylhydroxylamine, m.p. 80° (decomp.), obtained from 2,4-dinitro-anisole, and 2,6-dinitro-phenylhydroxylamine, m.p. 115° (decomp.) is obtained similarly (*Borsche*, Ber. 56, 1496). 3,5-Dinitro-phenylhydroxylamine,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{NHOH}$ , m.p. 135-137° has been prepared by *Cohen* (J. 87, 1257) by reducing *sym*-trinitrobenzene with  $\text{H}_2\text{S}$ . 2,4,6-Trinitro-phenylhydroxylamine, *picryl-hydroxylamine*,  $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{NHOH}$ , m.p. 113° (decomp.), prepared by *Borsche* (Ber. 56, 1492) from trinitro-phenetole and hydroxylamine hydrochloride, is oxidised by nitric acid to 1,2,3,5-tetranitrobenzene (p. 62). 3,5-Dinitro-*p*-tolylhydroxylamine, m.p. 135-136° obtained by *Anschütz* (Ber. 48, 152), by reducing 2,4,6-trinitrotoluene (p. 64) with ammonium sulphide in alcoholic solution, is oxidised to the corresponding azoxy-compound (*Brand*, Ber. 49, 673).

***o*-Nitro-phenylhydroxylamine**, m.p. 74° (decomp.) is obtained by the reduction of *o*-nitronitrosobenzene, or from *o*-dinitrobenzene by reduction with ascorbic acid. ***p*-Nitro-phenylhydroxylamine**, m.p. 107°, is obtained by the latter method from *p*-dinitrobenzene (*Kuhn, Weygand, Ber. 69, 1960*).

**Phenyl-hydroxyurethane**,  $C_6H_5N(OH)COOEt$ , m.p. 47.5°, obtained from phenylhydroxylamine by the action of chloroformic ester in ether, gives an oily methyl ether when treated with methyl iodide in alkaline solution (*Bamberger, Ber. 52, 1111*).

**DIARYL-HYDROXYLAMINES** have been prepared from nitroso-aryls and aryl-magnesium halides. They are not very stable, decomposing readily to diarylamines and diaryl nitrogen oxides. Their salts are coloured and are more stable than the free base (*Mejer, Ber. 54, 327*). **Diphenyl-hydroxylamine**, m.p. 60°. **Di-*o*-tolyl-hydroxylamine**, pale yellow crystals, m.p. 91-92° (decomp.) (*Wieland, Ber. 45, 494; 48, 1117*). Their oxidation products are free radicals and are discussed in Vol. IV.

**2,4-Dinitro-diphenylhydroxylamine**,  $(NO_2)_2C_6H_4N(OH)Ph$ , m.p. 114° (decomp.), orange needles, is formed from 1,2,4-bromo-nitrobenzene and phenylhydroxylamine, and also be the action of conc. sulphuric acid on tetranitro-tetra-phenylhydrazine. It forms reddish-brown salts with alkalis. It dissolves unchanged in conc.  $H_2SO_4$ , forming an intensely violet solution (*Wieland, Ber. 39, 3038*).

***p*-Nitroso-diphenylhydroxylamine**,  $NOC_6H_4N(OH)Ph$ , shiny bronze-coloured leaflets, m.p. 147-152° with rapid decomp., is formed by the action of conc.  $H_2SO_4$  on nitrosobenzene. If the *p*-position in nitrobenzene is occupied, say by chlorine, this is partly eliminated by the acid, and *p*-chloro-*p*'-nitroso-diphenylhydroxylamine is formed in greenish leaflets with a bronze lustre, m.p. 143° (decomp.). The deep-red salts and the methyl ester, m.p. 138°, which is derived from them have been allotted a quinoid structure,  $HON:C_6H_4:NOPh$ , but the evidence for this is slender. Boiling dilute  $H_2SO_4$  or NaOH decomposes *p*-nitroso-diphenylhydroxylamine with regeneration of nitrosobenzene (*Wieland, Ber. 39, 3036*).

#### (d) Aryl-nitrosohydroxylamines

**N-Phenyl-nitrosohydroxylamine**,  $C_6H_5N(OH) \cdot NO$  or  $C_6H_5NO(:NOH)$ , m.p. 59°, is produced: (1) from an ice-cold solution of phenylhydroxylamine in HCl by the action of  $NaNO_2$ , or from a solution in ammonia by the action of methyl or amyl nitrite (*Marvel, Am. 41, 270; Slater, J. 117, 587*); (2) by the action of hydroxylamine and sodium ethoxide on nitrobenzene (*Angeli, Atti. R. Accad. Lincei 8, II, 28*); (3) from nitrosoacetanilide (p. 111), or, together with the isomeric nitramine, from potassium benzene *n*-diazotate by oxidation with alkaline hydrogen peroxide (*Bamberger, Ber. 42, 3568, 3582*); (4) by passing nitric oxide into an ethereal solution of  $PhMgBr$  (*Sand, Ann. 329, 190*); (5) by acting upon nitrosobenzene with the sodium salts of nitrohydroxylaminic acid,  $HON:NO_2H$ , or benzene sulphhydroxamic acid (*Angeli, Gazz. 33, II, 239*). The ammonium salts, "cupferron," m.p. 164°, is used in analysis for separating certain metals. The sparingly soluble iron salt is characteristic (*Thornton, Sillman J. [7], 38, 137; Auger, C.r. 170, 995*). N-Phenyl-nitrosohydroxylamine is a very unstable substance, decomposing spontaneously into nitrosobenzene, benzene diazonium nitrate and other substances, such as 4,4'-dinitro-diphenylamine,  $NH(C_6H_4NO_2)_2$ .  $KMnO_4$  oxidises it instantly (*Angeli, Atti. R. Accad. Lincei 32, I, 443, 539*). By methylating its salts with methyl iodide, or the free substance with diazomethane, a methyl-ether, m.p. 38°, is obtained, probably derived from the same tautomeric form,  $PhNO(:NOH)$ , as the salts of phenyl nitrosohydroxylamine, since it is reduced by aluminium amalgam to diazobenzene methyl ether,  $PhN:NOMe$  (*Bamberger, Ber. 31, 537*). For complex salts of aryl-nitrosohydroxylamines see *Baudisch, Ber. 49, 172*. ***p*-Chloro- and *p*-bromo-N-phenyl-nitrosohydroxylamine**, m.p. 74.5° and 87°.

#### (e) Amino-derivatives or Anilines

The aromatic amino-compounds are derived from benzene and the alkyl-benzenes by replacing hydrogen by amino-groups:

$C_6H_5 \cdot NH_2$   
Aniline; aminobenzene

$C_6H_4(NH_2)_2$   
Phenylene-diamine;  
diamino-benzene

$C_6H_3(NH_2)_3$   
Triamino-benzene

On the other hand, they may be regarded as derivatives of ammonia, and hence primary, secondary, and tertiary aromatic amines exist:

$C_6H_5NH_2$   
Phenylamine

$(C_6H_5)_2NH$   
Diphenylamine

$(C_6H_5)_3N$   
Triphenylamine

$C_6H_5NHCH_3$   
Phenyl-methylamine

$C_6H_5N(CH_3)_2$   
Phenyl-dimethylamine

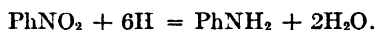
If the hydrogen in the side-chains of the benzene homologues is replaced by the  $NH_2$ -group, the compounds formed are true analogues of the aliphatic amines, e.g.,  $Ph \cdot CH_2 \cdot NH_2$ , benzylamine. They will be considered in connection with the alcohols from which they are derived.

The benzene ring and the nitrogen atom attached to it lie in one plane, but the two hydrogen atoms of the amino-group do not lie in the same plane, because of the non-planar distribution of the three nitrogen valencies. Hence the *p*-phenylene diamines and tetra-methyl-*p*-phenylene diamines have finite electric moments (*Weissberger, Williams, Sängewald, Z. physikal. Chem. B 5, 237*).

### 1. Primary Aromatic Amines

#### Methods of formation

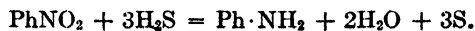
*I. Reduction.*—1. The most general method of preparation is by the reduction of the corresponding nitro-compounds:



N-Phenylhydroxylamines and nitrosobenzenes are intermediate products in this reduction, and can be isolated under suitable conditions (p. 59).

The more important methods of reduction are:

(a) The action of ammonium sulphide in alcoholic solution (*Zinin, 1842*):



With polynitro-compounds, this method usually only reduces one nitro-group and nitramino-compounds are formed. In chloro-nitrobenzenes, nitro-groups in the ortho-position to chlorine or to another nitro-group are not reduced by ammonium sulphide, but either chlorine or the nitro-group is replaced by S or SH (*Laubenheimer, Ber. 11, 1156; Beilstein, Ber. 11, 2056*). In general, nitro-groups in the *o*-position to other substituents are unaffected by ammonium sulphide, but in most cases are reduced by  $SnCl_2$  (*Cohen, J. 87, 1257*). In place of  $(NH_4)_2S$ , the sulphides, hydrosulphides, and polysulphides of the alkali metals can be used (see *Brand, J. pr. 74, 449*). Sodium disulphide,  $Na_2S_2$ , is a valuable reagent for this purpose and is oxidised to the thiosulphate:

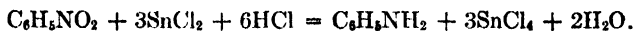
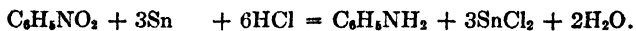


(b) The action of zinc and HCl on alcoholic solutions of nitro-compounds (*A. W. Hofmann*), or of iron filings and acetic acid or HCl



(*Bechamp*, 1852). Aniline and *o*- and *p*-toluidine are manufactured in this way industrially, iron and hydrochloric acid being used; for the mechanism of this reaction see p. 75. The use of zinc and HCl is to be avoided, since chloro-compounds are often formed.

(*c*) The action of tin and HCl (*Roussin*), or acetic acid (*Friedländer*, 1882), or of a solution of  $\text{SnCl}_2$  in HCl.



The last reaction may be used for the quantitative determination of nitro-groups. By adding the calculated quantity of  $\text{SnCl}_2$  in alcoholic HCl to the alcoholic solution of a polynitro compound, the reduction can be carried out step by step. In 2,4-dinitro-toluene the *p*- $\text{NO}_2$  is thus reduced, while ammonium sulphide reduces the *o*- $\text{NO}_2$  (*Anschutz*, 1886; *Schroeter*, *Ber.* 35, 2073). Graphite accelerates the reduction with Sn and HCl (*Pinnow*, *J. pr.* 65, 579). *Losner* (*Z. physikal. Chem.* 56, 1) has determined the speed of reduction with  $\text{SnCl}_2$  and HCl.

(*d*) Electrolytic reduction in acid solution. In concentrated sulphuric acid, *p*-aminophenol is the chief product, being produced by a rearrangement of  $\beta$ -phenylhydroxylamine which is first formed (p. 69). For summary of literature see *Ann.* 355, 175. For partial electrochemical reduction of polynitro-compounds see *J. pr.* 87, 487.

Other reducing agents used with advantage in certain cases are:

(*e*)  $\text{TiCl}_3$  and HCl, especially for the quantitative determination of nitro-groups (*Knecht*, *Ber.* 36, 1554; see *Knecht* and *Hibbert*, "New Reduction Methods in Volumetric Analysis," London, 1925, p. 29).

(*f*) Sodium arsenite (*Losner*, *J. pr.* 50, 563).

(*g*) Zinc dust in ammoniacal or alcoholic solution.

(*h*) Ferrous compounds, such as  $\text{Fe}(\text{OH})_2$ ,  $\text{FeCO}_3$ , ferrous acetate (*Ger. Pat.* 418,497).

(*i*) Propyl-, isopropyl-, butyl-, or isoamyl alcohol and NaOH (*Suter*, *Ann.* 50, 2733).

(*j*)  $\text{FeSO}_4$  and baryta water or ammonia is useful for reducing nitro-compounds which are soluble in water or alkalis (*Gabriel*, *Ber.* 15, 2237; *Fischer*, *Ber.* 28, 3193).

(*k*) Hydrogen reduces nitro-compounds smoothly to anilines when the reactants are passed over finely divided metals, such as Cu, Ni, etc., at 200–400° (*Sabater*, *Senderens*, *C.r.* 133, 321) or over metallic oxides such as  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$  (*Ger. Pat.* 272,322). In the presence of finely divided metals, especially Fe, Pt, and Pd, the reduction can be carried out in alcohol or ether, at ordinary or somewhat higher temperatures, with or without the application of pressure (*Br. Pats.* 295,824 and 297,212; *Paal*, *Ber.* 40, 2209).

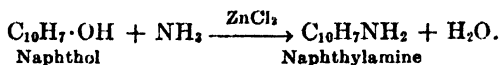
(*l*)  $\text{CO}$ , in the presence of iron, at 150° and 150 atm. reduces nitrobenzene to aniline.

2. Reduction of nitroso-compounds, see nitroso-benzene (p. 67), nitroso-dimethylaniline (p. 105), and quinone-oximes.

3. Reduction of hydrazo-compounds and hydrazines (pp. 144, 149).

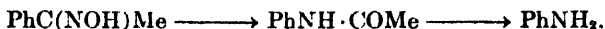
II. Exchange reactions.—Halogens,  $\text{NO}_2$ , OH and alkoxy groups can be replaced by  $\text{NH}_2$  by the action of ammonia. Pure halogenated benzenes when heated in ammonia yield only traces of amino-compounds, but in the presence of small quantities of copper salts the reaction takes place more readily (*Ger. Pat.* 204,951). Compounds containing a nitro-group react without a catalyst, and the more readily the greater the number of nitro-groups. 1,2-Chloro- or -bromonitrobenzene, 1,2-dinitrobenzene, 2-nitrophenol and its alkyl ethers, 4-chloro- or -bromo-nitrobenzene, 4-nitrophenol and its alkyl ethers, all give nitramino-compounds when heated with ammonia. The meta-compounds do not react (*Barr*, *Ber.* 21, 1541).

Phenols can be directly converted into primary (and secondary) amines by heating with  $\text{ZnCl}_2 \cdot \text{NH}_3$  to 300–350° (*Calm*, *Ber.* 16, 2812; *Buch*, *Ber.* 17, 2633; *Merz*, *Ber.* 19, 2916; *Lloyd*, *Ber.* 20, 1254). Naphthols react in the same way but much more easily:

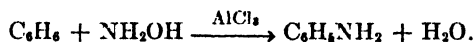


5. Halogen derivatives or alkali sulphonates can be heated with sodamide (*Sachs*, Ber. 39, 3006).

6. The carboxyl group of aromatic acids is replaced by  $\text{NH}_2$  as with the aliphatic acids by Hofmann's method, through the amides, and by Curtius' method through the azides. The direct method, using hydrazoic acid, can also be used (*v. Braun*, Ann. 490, 125; *Osterlin*, Z. angew. Chem. 1932, 45, 536). A further method is the Beckmann rearrangement of the oximes of aromatic ketones to acylated aromatic amines (Vol. I, p. 268), from which the amines are obtained by hydrolysis:

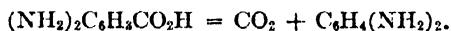


7. The direct introduction of the amino-group into benzene hydrocarbons may sometimes be effected by heating the latter with hydroxylamine hydrochloride and  $\text{AlCl}_3$  or  $\text{FeCl}_3$  (*Graebe*, Ber. 34, 1778).

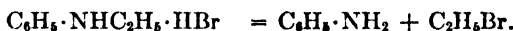
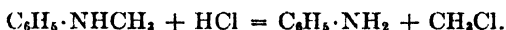


The yield of anilines is poor, and is still lower in the catalytic reaction of benzene with ammonia at higher temperatures (*Wibaut*, Ber. 50, 541).

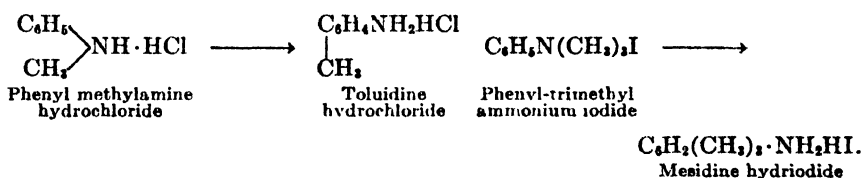
III. *Decomposition reactions.*—8. Heating amino-carboxylic acids:



9. Heating secondary or tertiary amines with  $\text{HCl}$ , or rapidly heating the quaternary ammonium salts alone: /



IV. *Reactions involving the benzene nucleus.*—10. When aniline is heated with methyl chloride, monomethyl aniline hydrochloride is the primary product; it dissociates at a higher temperature, aniline and methyl chloride being re-formed. But at a still higher temperature ( $340^\circ$ ) a nuclear hydrogen atom of aniline is replaced by a methyl group, and a toluidine hydrochloride is obtained. Phenyl-trimethylammonium iodide gives mesidine hydriodide:



In this way secondary and tertiary aromatic bases can be converted into isomeric primary bases. Instead of the hydrohalides of secondary and tertiary bases, the salts of primary bases can be heated to  $300^\circ$  with the appropriate alcohols (*Hofmann*, 1880; Ber. 13, 1729); or the free bases are heated to  $250^\circ$  with paraffin alcohols and zinc chloride. The corresponding phenols are by-products in this reaction, *e.g.*, mesitol,  $\text{C}_6\text{H}_2\text{Me}_3\text{OH}$ , together with mesidine,  $\text{C}_6\text{H}_2\text{Me}_3\text{NH}_2$ . The greater the number of methyl groups attached to the ring the

more the phenols predominate; pentamethyl-aniline is not formed at all, but only pentamethyl-phenol.

Similar apparent migrations of substituents from the amino-group to the nucleus have been observed in other cases, *e.g.*, by *de Brereton, Evans*, *Proc.* 1895, 235; see also phenylhydroxylamine *etc.*, p. 69.

11. The oximes of some ketones derived from unsaturated cyclohexenes, such as those of methyl- and dimethyl-cyclohexenone, trimethyl-cyclohexenone, or isoacetophorone, yield primary anilines when heated with HCl, atomic rearrangement taking place (*Ann.* 322, 379).

12. Small yields of anilines have been obtained by acting on phenyl magnesium halides with monochloramine (*Coleman, Am.* 50, 1193), or with hydroxylamine (*Weissberger, J. pr.* 124, 29).

*Properties and reactions of the aromatic amines.*—The simpler primary amines are colourless compounds of a peculiar, and not unpleasant smell. They can be distilled without decomposition at ordinary pressure. In salt formation they resemble alkylamines (Vol. I), but they are much weaker bases than the primary alkylamines, have no alkaline reaction, and are only slightly soluble in water. They are volatile with steam. The primary bases can be separated from the secondary and tertiary bases by the aid of ethyl oxalate, which combines with the primary bases to give high-boiling oxamino-esters, which are easily separated from the other, low-boiling, bases by distillation (*Thomas, J.* 111, 562).

The basicity of substituted phenylamines is still further reduced when the substituents are acidic in character. Thus, the salts of disubstituted anilines, such as  $C_6H_3Cl_2 \cdot NH_2$  and  $C_6H_3(NO_2)_2 \cdot NH_2$ , are decomposed by water, or do not exist at all.

The aromatic amines are hydrogenated to the corresponding amino-cyclohexanes (Vol. II, p. 106) by passing their vapours with hydrogen over finely divided nickel at  $190^\circ$ , or by heating them with hydrogen under high pressure in the presence of nickel. The amino-cyclohexanes are as basic as the aliphatic amines, and do not resemble the aromatic amines.

As the representative of the primary aromatic amines aniline will be described in some detail. The following are the general reactions of the amino-group:

1. Alkali metals dissolve in primary aromatic amines on heating, with liberation of hydrogen. Aniline gives potassium and dipotassium derivatives,  $PhNHK$  and  $PhNK_2$  (p. 78).

2. Alkyl halides combine with the anilines to give secondary, tertiary, and finally *quaternary ammonium compounds* (Vol. I, p. 197). When passed over silica gel at  $365-400^\circ$ , mono- and di-alkyl-anilines are formed (*Brown, Reid, Am.* 46, 1836).

3. One molecule of an aldehyde combines with one or two molecules of a primary amine, with elimination of water (*Miller, Ber.* 25, 2020). With furfural, all primary anilines form intensely red compounds. With one molecule of a ketone analogous condensation products of the type  $R \cdot N=CR_2$ , called anils, are obtained.

4. The reactions of free primary anilines and their salts with

nitrous acid have been of paramount importance in the development of organic chemistry. The compounds formed are called *diazo-compounds*. They are intermediate steps in the conversion of nitro- and amino-compounds into substitution products of many kinds.

5. With thionyl chloride, the primary anilines react in the same way as the primary aliphatic amines (Vol. I, p. 193). Thionyl-anilines are formed.

6. One hydrogen atom in the amino-group is very readily replaced by an acid radical, and acid anilides, corresponding to the acid amides (Vol. I, p. 321), are formed. The acetyl-compounds usually crystallise well, and are often prepared as characteristic derivatives (p. 88; *Jacobs*, *Ann.* **39**, 1439).

7. In the same way as the primary aliphatic amines (Vol. I, p. 195), the primary anilines give *carbylamines*, or *isonitriles*, with chloroform and aqueous alkali.

8. With carbon disulphide the primary anilines give  $H_2S$  and *diaryl-thioureas*, while the primary aliphatic amines give the ammonium salts of alkyl-dithiocarbamic acids (Vol. I, p. 195).

9. *Quinoline* and other bases containing quinoline nuclei have been synthesised by heating aniline and other aromatic bases with glycerol, sulphuric acid, and nitrobenzene, or some other oxidising agent. These syntheses have greatly contributed to the development of the chemistry of the quinoline group. Other syntheses of quinoline derivatives depend on the condensation of primary aromatic amines with aliphatic aldehydes by means of  $HCl$  or  $ZnCl_2$ .

10. Primary aromatic amines when heated with  $\alpha$ -halogeno-ketones gives *indoles*, and sometimes *dihydro-pyrazine* derivatives. The hydrohalides of the anilines combine with stannic halides to give chloro- and bromo-stannates which crystallise readily (*Maier*).

**Aniline**, *phenylamine*, *aminobenzene*,  $C_6H_5NH_2$ , m.p.  $-8^\circ$ , b.p.  $184^\circ$ ,  $d_4$  1.0361, is an oil with a characteristic smell, soluble in 31 parts of water at  $12.5^\circ$ ; dipole moment 1.55 D.; Raman spectrum see *Dadieu*, *Mo.* **52**, 379; *Kohlbrausch*, *Mo.* **57**, 225.

*History*.—Aniline was discovered in 1826 by *Unverdorben*, among the distillation products of indigo, and was called *crystallin* by him, because its salts crystallise readily. *Runge* (1834) detected it in coal-tar and called it *kyanul*, on account of the blue colour it gives with bleaching powder. *Fritzsche* (1841) while distilling indigo with caustic potash found a base which he called aniline from the Spanish word for indigo, *anil*. *Zinin*, in the same year, 1841, reduced nitrobenzene with ammonium sulphide and called the product *benzidam*. The fact that these four bases are identical was shown by *Hofmann* (*Ann.* **47**, 37).

Industrially aniline is made from nitrobenzene by reduction with iron in presence of one-fortieth of the quantity of  $HCl$  required by the equation:



The first product is probably  $FeCl_2$  which acts as a carrier in the reduction of nitrobenzene by iron and water, the finely divided metal being the actual reducing agent (*Wohl*, *Ber.* **27**, 1436, 1815).

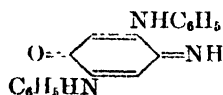


The catalytic reduction of nitrobenzene with hydrogen is at present carried out on a very large scale. Aniline is also produced from chlorobenzene vapour by heating with ammonia in the presence of catalysts (Chem. tech. Übers. 57, 159).

Other reagents for reducing nitrobenzene to aniline have been given above (p. 71), and the general methods of formation of primary phenylamines have been summarised on p. 71, mainly by reference to aniline. The same applies to the reactions of aniline: the action of alkali metals, alkyl halides, aldehydes, nitrous acid, thionyl chloride, the formation of anilic acids, the reaction with  $\text{CS}_2$ , chloroform and caustic potash, glycerol and nitrobenzene, etc. Aniline, which is readily available, is used as a starting material for the preparation of many aromatic compounds, almost as much as ammonia itself. In spite of its feeble basicity, it precipitates zinc, aluminum, and ferric hydroxides from solutions of their salts, and it displaces ammonia from its salts because it is less volatile.

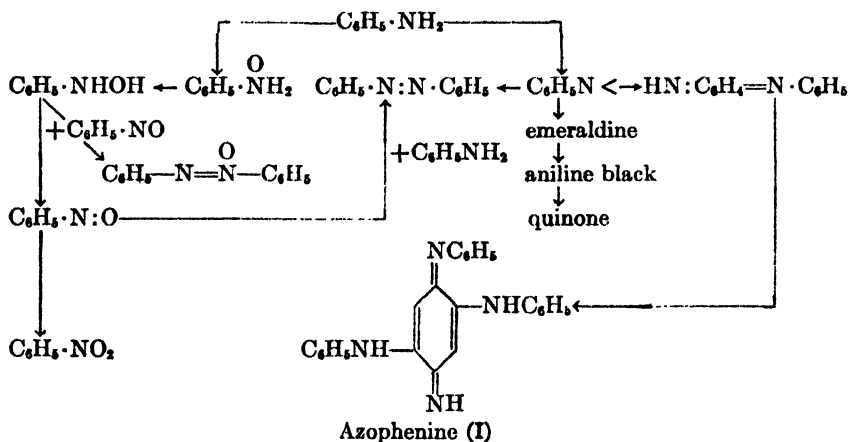
Aniline is a poison; for its poisonous effects see *Adamson*, Ind. Eng. 8, 1058. It is a solvent for many substances, e.g., indigo.

Aniline is very sensitive to oxidation. In air it gradually turns brown and resinifies. An aqueous solution of bleaching powder produces a purple-violet colour (*Nietzki*, Ber. 27, 3263). With sulphuric acid and a few drops of potassium chromate solution it first turns red and then intensely blue. On oxidation with hot bleaching powder solution, or cold permanganate solution, it passes through a series of intermediate stages and is finally reconverted, in part, into nitrobenzene (*Bamberger*, Ber. 26, 496; 31, 1522). With chromic acid it gives quinone (p. 235) and with chlorates in presence of certain metallic salts it gives *aniline black* (p. 246). Persulphates oxidise it to 2,5-dianilido-quinone-monimine,

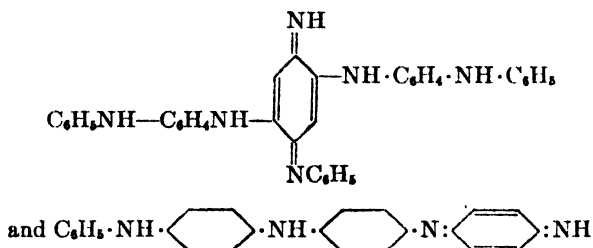


and bromic acid produces amino-anilido-quinone-monimine, m.p. 127–128° (C. 1911, I, 614). On catalytic reduction aniline is converted into cyclohexylamine (*Adkins*, Am. 52, 4349; C. 1931, I, 918; C. 1931, II, 3109).

The researches of *Bamberger*, *Willstätter*, and *Goldschmidt* have shown that three main types of oxidation products of aniline may be distinguished: monomolecular, such as phenyl-hydroxylamine and nitrobenzene; dimolecular, such as azobenzene, azoxybenzene, and phenyl-quinone-diimine; and polymolecular, such as emeraldine and aniline black (Ber. 53, 36; 55, 3223). *Goldschmidt* has represented these relations by the scheme reproduced below, in which the substances on the same line belong to the same type of oxidation:

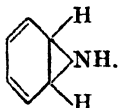


It is probable that with certain oxidising agents aniline oxide, and with others the radical  $\text{PhN}\cdot$ , are the primary oxidation products. The compounds which are related to phenyl-quinone-diimine belong to the same stage of oxidation of the radical and are formed either by the hydrolysis of that compound or from dianilino-N-phenyl-quinone-diimine (I above); such substances are



and aniline black itself (p. 246).

Aniline and nitrosobenzene (p. 67) combine to give azobenzene; aniline and nitrobenzene in the presence of powdered caustic potash give azobenzene and phenazine oxide (*Wohl*, Ber. 34, 2442). *Schmidt* (Ber. 55, 1581) describes a compound obtained from aniline and sulphuryl azide,  $\text{SO}_2(\text{N}_3)_2$ , which he calls pseudó-aniline, and which is possibly represented by the formula



Many important dyes, such as aniline black, fuchsin, and many others, and drugs such as antifebrin, antipyrin, etc., are made from aniline, as well as certain plastics (Br. Pats. 266,358 and 306,972; U. S. Pat. 1,756,818).

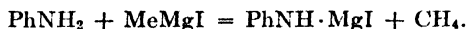
**ANILINE SALTS.** The hydrochloride, m.p. 198°, commercially known as "aniline salt," is obtained in the pure, dry form when dry HCl is passed into a solution of aniline in ether (*Ullmann*, Ber. 31, 1698). It deliquesces in air. For anomalous salts of aniline with HCl and HBr see *Maudslayi*, Ber. 53, 2216. Its double salt with platinum chloride crystallises from alcohol in yellow needles.

*Double salts with stannous and stannic chlorides*,  $\text{SnCl}_2 \cdot 2\text{PhNH}_2 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$  and  $\text{SnCl}_4 \cdot 2\text{PhNH}_2 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ . *Sulphate*,  $(\text{PhNH}_2)_2\text{H}_2\text{SO}_4$ . *Thiosulphate*,  $(\text{PhNH}_2)_2\text{H}_2\text{SO}_3$ ; only primary anilines form normal thiosulphates (*Wahl*, C.r. 133, 1215). *Nitrate*, rhombic plates. *Perchlorate*, brown elongated plates, readily soluble in water, stable in air, and explosive (*Spallino*, Ann. chimia. appl. 1, 435). *Oxalate*, rhombic prisms. Not only the hydrochloride, but also free aniline forms double salts with some salts. In a similar way it adds on to trinitrobenzene.

**POTASSIUM-ANILINES.**  $\text{PhNHK}$  and  $\text{PhNK}_2$  are not known in the free state, but the formation of di- and triphenylamines in the action of bromobenzene on the reaction product of potassium and aniline may indicate that the hydrogen of the amino-group is replaced by potassium. Sodium does not act on aniline below  $200^\circ$ . Small quantities of  $\text{Cu}$ ,  $\text{CuO}$ , etc., accelerate this reaction (*Ger. Pat.* 215,339). See also acetanilide, p. 88, and monomethylaniline, p. 81.

In the isotope exchange between aniline hydrochloride and heavy water not only are the three hydrogen atoms of the  $-\text{NH}_3^+$  group exchanged for deuterium, but also three of the nuclear hydrogen atoms, those in the *o*- and *p*-positions (*Harada, Titani*, Bull. Chem. Soc. Japan 11, 554).

**ANILINE MAGNESIUM HALIDE COMPOUNDS**, such as  $\text{PhNHMgI}$ , are obtained as crystalline precipitates when aniline reacts with an ethereal solution of an alkyl magnesium halide (*Meunier*, C.r. 136, 758).



They rapidly absorb  $\text{CO}_2$  with formation of carbamates (*Houben*, Ber. 37, 3978) and with esters give acid anilides (*Bodrour*, C.r. 142, 101). **Magnesium aniline**,  $\text{Mg}(\text{NHPh})_2$ , is a golden-yellow powder which decomposes in air, and is obtained by passing aniline vapour over  $\text{Mg}$  at  $370^\circ$ . It adds on  $\text{CO}_2$  with the formation of magnesium phenyl-carbamate,  $\text{Mg}(\text{OCONHPh})_2$  (*Terentiev*, Bull. 35, 1164).

**AMINOTOLUENES, TOLUIDINES.** Some compounds belonging to this class are important in the dye industry, especially *o*- and *p*-toluidines. Most of these bases are liquid at ordinary temperatures, and readily give crystalline acetyl compounds on boiling with acetic acid or treatment with acetyl chloride or acetic anhydride. These substituted acetamides form well-defined crystals of constant melting point and can be used with advantage for the characterisation of the bases, from which they are easily prepared. In the following sections the m.p. of the acetyl compound is given for each base in addition to the m.p. or b.p. of the base itself. The toluidines are prepared by the reduction of nitro-compounds and also by heating the hydrochlorides of *N*-methylated bases such as dimethyl-aniline,  $\text{PhNMe}_2$ , under pressure at high temperatures (p. 73) (*Hickinbottom*, J. 1930, 1558).

**TOLUIDINES**,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4\text{NH}_2$ . The three toluidines are isomeric with benzylamine,  $\text{PhCH}_2\text{NH}_2$ , which will be dealt with in connection with benzyl alcohol, and with methyl-aniline,  $\text{PhNHMe}$  (p. 81). They are prepared by the reduction of the three nitro-toluenes (p. 63). *m*-Toluidine can also be prepared by reduction of *m*-nitrobenzal chloride, which is obtained from *m*-nitrobenzaldehyde (*Ehrlich*, Ber. 15, 2009; *Harz*, Ber. 18, 3398). *p*-Toluidine was discovered in 1845 by *Hofmann* and *Muspratt*.

*o*-Toluidine is dimorphous, m.p.  $-16.25^\circ$  and  $-24.4^\circ$ ; b.p.  $199^\circ$  (*Timmermans*, Belg. 30, 62); acet-*o*-toluidide, m.p.  $110^\circ$ , b.p.  $296^\circ$ . *m*-Toluidine, liquid, b.p.  $203^\circ$ ; acet-*m*-toluidide, m.p.  $65^\circ$ , b.p.  $303^\circ$ . *p*-Toluidine, m.p.  $45^\circ$ , b.p.  $200^\circ$ ; acet-*p*-toluidide, m.p.  $145^\circ$ , b.p.  $306^\circ$ .

*p*-Toluidine forms a monohydrate,  $\text{MeC}_6\text{H}_4\text{NH}_2 \cdot \text{H}_2\text{O}$ , m.p.  $42.5^\circ$ , which can be used for isolating and purifying the base (*Friswell*, Chem. and Ind. 27, 258).

The hydrochlorides of *o*-, *m*-, and *p*-toluidine melt at 215°, 228°, and 243°, respectively, and boil without decomp. at 242°, 250°, and 257° (Ullmann, Ber. 31, 1698).

*Separation of o- and p-toluidine.*—On nitration of toluene *o*- and *p*-nitrotoluenes are formed. These, when reduced, give the industrially important toluidines. The *o*- and *p*-toluidines are separated by treating a mixture of the bases with less sulphuric acid than is required for neutralisation and distilling. The *p*-compound is the stronger base, and remains as the sulphate. The greater solubility of *o*-toluidine oxalate or of acet-*o*-toluidine can also be used with advantage. A further method of separating aniline, *o*-, and *p*-toluidine is based on the different behaviour of their hydrochlorides with  $\text{NaH}_2\text{PO}_4$  (Lewy, Ber. 19, 1718, 2728; Dobriner, Z. anal. Chem. 34, 734).

In the aniline dye industry a distinction is made between: *aniline oil for blue* = pure aniline; *aniline oil for red* = equimolecular proportions of aniline, *o*-, and *p*-toluidine; *aniline oil for safranin* = aniline and *o*-toluidine, obtained from the distillate of the fuchsin melt.

The free toluidines are readily oxidised to azo-compounds (Green, Ber. 26, 2772). When the amino-group is protected from oxidation by the presence of an acid radical, *e.g.*, acetyl,  $\text{KMnO}_4$  oxidises the methyl group to carboxyl; thus, acet-*o*-toluidine is converted into *o*-aceto-aminobenzoic acid (Bedson, Ber. 14, 263). When the acet-toluidines are chlorinated, brominated, or nitrated the new substituent as a rule goes into the *p*- or *o*-position to the acetamino group (see p. 14).

*o*-Toluidine gives a violet colour with aqueous bleaching powder and  $\text{HCl}$ , like aniline, but *p*-toluidine does not. From a solution of *o*-toluidine in  $\text{HCl}$ ,  $\text{FeCl}_3$  precipitates a blue substance, known as *toluidine blue*. With *n*-butyl chloride, *p*-toluidine gives mono- and di-butyl-toluidines, but *o*-toluidine gives only a mono-derivative, possibly for steric reasons.

**XYLIDINES**,  $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NH}_2$ . All six possible isomers are known:

- 3-Amino-*o*-xylene, *v-o*-xylidine, liquid, b.p. 223°, acetyl deriv. m.p. 134°.
- 4-Amino-*o*-xylene, *as-o*-xylidine, m.p. 51°, b.p. 226°, acetyl deriv. m.p. 99°.
- 2-Amino-*m*-xylene, *v-m*-xylidine, liquid, b.p. 216°, acetyl deriv. m.p. 177°.
- 4-Amino-*m*-xylene, *as-m*-xylidine, liquid, bp. 212°, acetyl deriv. m.p. 129°.
- 5-Amino-*m*-xylene, *sym-m*-xylidine, liquid, b.p. 220°, acetyl deriv. m.p. 138°.
- 3-Amino-*p*-xylene, *p*-xylidine, m.p. 15°, b.p. 215°, acetyl deriv. m.p. 139°.

For the melting and boiling points of the hydrochlorides see Ullmann, Ber. 31, 1699.

Commercial xylidine is obtained from crude xylene and is used for making azo-dyes; it consists mainly of *as-m*- and *p*-xylidines. For the separation of the isomeric xylidines see Noelting, Ber. 18, 2664; Staedel, *ibid.* 2918.

**AMINO-POLYMETHYL-BENZENES**,  $(\text{CH}_3)_n\text{C}_6\text{H}_{6-n}\text{NH}_2$ . A product has been obtained industrially by heating xylidine hydrochloride and methyl alcohol at 250° under pressure. It consists mainly of *sym*-pseudocumidine and mesidine, and is used for making red azo-dyes (Hofmann, Ber. 15, 2895).

*sym*-Pseudocumidine,  $[\text{5NH}_2, 1,2,4]$  m.p. 68°, b.p. 235°; acetyl deriv. m.p. 164° (Haller, Ber. 18, 89; Auwers, Ber. 18, 2661).

Mesidine,  $[\text{2NH}_2, 1,3,5]$ , liquid, b.p. 233°; acetyl deriv. m.p. 216° (Engel, Ber. 18, 2229; Feil, Ber. 24, 3546).

Duridine,  $[\text{3NH}_2, 1,2,4,5]$ , m.p. 75°, b.p. 261–262°; acetyl deriv. m.p. 207° (Willstätter, Ber. 42, 4160).

Isoduridine,  $[\text{4NH}_2, 1,2,3,5]$ , m.p. 23°, b.p. 258–260°; acetyl deriv. m.p. 217.5° (Hey, J. 1931, 1581).

Amino-tetramethyl-benzene,  $[\text{5NH}_2, 1,2,3,4]$ , m.p. 70°, b.p. 260°; acetyl deriv. m.p. 172° (Limpach, Ber. 21, 644; Töhl, 21, 305).

Amino-pentamethyl-benzene, m.p. 151°, b.p. 277°; acetyl deriv. m.p. 213° (Hofmann, Ber. 18, 1821).



**HOMOLOGUES OF ANILINE WITH LARGER ALKYL RADICALS.** These are prepared from nitro-compounds by reduction, and can also be obtained by the apparent rearrangements which take place when aniline is heated with aliphatic alcohols and  $\text{ZnCl}_2$  at  $250\text{--}280^\circ$  (see p. 73). The alkyl group goes into the *p*-position to  $\text{NH}_2$ . With isobutyl and isoamyl alcohols, *p*-tert.-butyl and *p*-tert.-amyl anilines are formed (*Anschütz*, Ber. 28, 407).

*p*-Amino-ethyl-benzene, m.p.  $-5^\circ$ , b.p.  $216^\circ$  (*Pictet*, Ber. 22, 1849).

*p*-Amino-propyl-benzene, b.p.  $225^\circ$ ; acetyl deriv. m.p.  $96\text{--}96.5^\circ$  (*Hickinbottom*, J. 1930, 1558, 1566).

*p*-Amino-isopropyl-benzene, b.p.  $225^\circ$ ; acetyl deriv. m.p.  $102^\circ$  (*Crystall*, Ber. 21, 1159).

*p*-Amino-isobutyl-benzene, b.p.  $235\text{--}236^\circ$ .

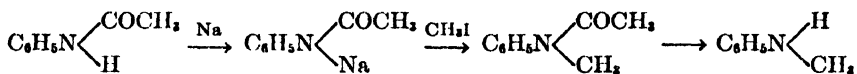
*p*-Amino-tert.butyl-benzene, m.p.  $17^\circ$ , b.p.  $228\text{--}230^\circ$ ; acetyl deriv. m.p.  $172^\circ$ .

*p*-Amino-octyl-benzene, m.p.  $19^\circ$ , b.p.  $310^\circ$ ; acetyl deriv. m.p.  $93^\circ$  (*Biran*, Ber. 18, 131).

## 2. Secondary and Tertiary Aromatic Amines and Quaternary Ammonium Bases

**N-ALKYL ANILINES.** *Methods of formation.*—1. The N-alkyl derivatives of aniline and of its homologues are formed, like the aliphatic amines (Vol. I), by the action of alkyl bromides or iodides on the primary bases, sometimes even in the cold. When mixed halides are used, addition of sodium carbonate is useful (U. S. Pat. 1,854,553). They can also be obtained by heating aniline hydrochloride or, preferably, hydrobromide (*Staedel*, Ber. 19, 1939) with alcohols to  $250^\circ$ , or by passing these compounds as vapours over  $\text{Al}_2\text{O}_3$  at  $400^\circ$ .

2. The above method gives a mixture of the hydrohalides of the mono- and di-alkylamines. The mono-alkylamines are prepared pure from the acetyl compounds of primary bases. These are dissolved in toluene or xylene and an equivalent quantity of sodium is added. Hydrogen is evolved and a solid, white, sodium-acetanilide is formed. This reacts smoothly with alkyl halides. The alkyl-acetanilide is then hydrolysed to the N-alkyl-aniline:



*Separation of primary, secondary, and tertiary amines.*—Tertiary amines can be obtained from a mixture of all three types of amines by treatment with acetic anhydride, with which the tertiary compounds do not react; the other types form non-basic acetyl derivatives. Secondary amines can be obtained pure by treating the mixture dissolved in hydrochloric acid with  $\text{NaNO}_2$ . The secondary compounds form N-nitroso-derivatives which are non-basic and insoluble in water, while the primary compounds give soluble diazonium salts, and the tertiary compounds C-nitroso-compounds which are basic. The nitrosamine can be reconverted into the secondary amine by boiling with hydrochloric acid, by reduction with Sn and HCl, or, best of all, by treating it in hydrochloric acid solution with thiourea (*Macmillan*, Read, J. 1929, 585), or with cuprous or ferrous chloride (*Jones*, Kenner, J. 1932, 711). The three types can be separated from one another by treating their alcoholic solution successively with small amounts of conc. sulphuric acid (*Price*, Chem. and Ind. 37, 82).

*Properties and reactions.*—The more important compounds of this class are the methyl- and ethyl-anilines. When freshly distilled,

they are colourless liquids, with a high refractive index, but they gradually turn brown on exposure to light. They smell somewhat like aniline, but are more unpleasant.

The behaviour of **secondary N-alkylamines** recalls that of dialkylamines (Vol. I, p. 193). *a.* They form salts, and combine with alkyl halides to give hydrohalides of tertiary amines. *b.* By the action of acid chlorides and anhydrides the imino-hydrogen is replaced by the acyl group. The same compounds are obtained by method of formation 2 (above). *c.* With nitrous acid they give nitrosamines.

In the **TERTIARY N-DIALKYL ANILINES** which contain a hydrogen atom in the *p*-position to the dialkylamino-group, this hydrogen is remarkably reactive. A number of reactions take place which are impossible, or difficult, with primary or secondary anilines. Nitrous acid converts them into *p*-nitroso-compounds. With formaldehyde, phosgene, and aromatic aldehydes the dialkyl anilines condense to form diphenylmethane derivatives.

The primary, secondary, and tertiary aromatic amines differ in their behaviour towards nitrous acid in the following ways:

1. Primary anilines give diazo- and diazoamino-compounds.
2. Secondary N-alkylanilines give nitrosamines.
3. Tertiary N-dialkylanilines give *p*-nitroso-compounds.

Other reactions of N-dialkylanilines are mentioned in connection with dimethylaniline.

The methyl- and ethyl-anilines have the following physical properties:

| Compound                   | M.p.                              | B.p.   | d.              |
|----------------------------|-----------------------------------|--------|-----------------|
| Monomethyl-aniline         | Liquid                            | 194°   | 0.939 (20°)     |
| Dimethyl-aniline           | 1.5°                              | 193°   | 0.9575 (20°/4°) |
| Ethyl-aniline              | Liquid                            | 206°   | 0.964 (15°)     |
| Diethyl-aniline            | -21.3° and -34.4°<br>(dimorphous) | 215.5° | 0.939 (15°)     |
| <i>n</i> -Propyl-aniline   | 222°                              |        |                 |
| Acetyl derivative          | 48-49°                            |        |                 |
| <i>iso</i> -Propyl-aniline | 212-213°                          |        |                 |
| Acetyl derivative          | 42°                               |        |                 |
| <i>n</i> -Butyl-aniline    | 241-242°                          |        |                 |
| Acetyl derivative          | 275°                              |        |                 |
| <i>iso</i> -Butyl-aniline  | 231-232°                          |        |                 |
| Acetyl derivative          | 273°                              |        |                 |

The N-methyl-anilines are used industrially for obtaining various dyestuffs. They are made by heating aniline hydrochloride and methyl alcohol to 220°, or by passing methyl chloride into boiling aniline.

**Methylaniline**,  $C_6H_5NHCH_3$ , is also produced by reducing *phenylcarbylamine* (p. 90) or *formaldehyde-aniline* (p. 84) (Frankland, J. 115, 198). The hydrochloride, m.p. 122°, is precipitated from the ethereal solution of the base by dry HCl (Scholl, Ber. 30,

3134). It gives no colour with bleaching powder solution. At  $330^{\circ}$  it is converted into toluidine. Methylphenylnitrosamine, see p. 111; methylacetanilide, see p. 89.

When oxidised with  $\text{H}_2\text{O}_2$  or permonosulphuric acid, methyl- and ethyl-aniline lose their alkyl groups and N-phenylhydroxylamine, nitrosobenzene, nitrobenzene, azoxybenzene, azobenzene, *etc.*, are formed (*Bamberger*, Ber. **35**, 703).

With formaldehyde and HCl, methyl- and ethyl-aniline form  $\text{PhNMe}\cdot\text{CH}_2\text{Cl}$  and  $\text{PhNEt}\cdot\text{CH}_2\text{Cl}$ , respectively. These can be reduced to dimethyl- and methylethylaniline (*Goldschmidt*, Ch. Ztg. **26**, 606; **28**, 1229; *Lemoult*, C.r. **139**, 978).

**DIMETHYLANILINE**,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ , m.p.  $2^{\circ}$ , is also formed on heating bromo- or iodobenzene with dimethylamine to  $250$ – $260^{\circ}$ . With dry HCl it gives a mono- and a di-hydrochloride,  $\text{PhNMe}_2\cdot\text{HCl}$  and  $\text{PhNMe}_2\cdot 2\text{HCl}$ , crystalline substances which deliquesce in air, and readily lose HCl (*Scholl*, Ber. **30**, 3134). Hydriodide, m.p.  $112^{\circ}$ . For the purification of dimethylaniline from aniline and methyl-aniline with formic acid, see *Ritter*, Ind. Eng. Chem. **28**, 33. Dimethylaniline gives no colour with hypochlorites. It combines with methyl iodide to form trimethylphenylammonium iodide,  $\text{PhNMe}_3\text{I}$ . With nitrous acid it gives *p*-nitroso-dimethylaniline (p. 105), and with nitric acid, *p*-nitrodimethylaniline. The same two compounds are formed with nitrosylsulphuric acid (*Biehringer*, Ber. **49**, 1405). With acetyl bromide and benzoyl bromide dimethylaniline yields acetyl- and benzoyl-monomethyl-aniline and some trimethylphenylammonium bromide (*Staedel*, Ber. **19**, 1947). Hydrogen peroxide or permonosulphuric acid oxidises it to dimethylaniline oxide (p. 83).

Dimethylaniline can be used in a number of condensation reactions. It combines with chloral to give a derivative of *p*-aminomandelic acid,  $\text{Me}_2\text{N}[4]\text{C}_6\text{H}_4[1]\text{CH}(\text{OH})\cdot\text{CCl}_2$ ; with phosgene to give tetramethyl-diaminobenzophenone,  $(\text{Me}_2\text{N}[4]\text{C}_6\text{H}_4[1])_2\text{CO}$ ; with orthoformic ester and zinc chloride to give hexamethyl-*p*-leucaniline,  $\text{CH}(\text{C}_6\text{H}_4\text{NMe}_2)_3$ ; with benzotrichloride to give malachite green (p. 532).

The homologous mono- and dialkylanilines behave similarly. The following may be mentioned:

**Methylethylaniline**,  $\text{PhNMeEt}$ , b.p.  $201^{\circ}$ . Its compound with methyl iodide is identical with that formed from dimethylaniline and ethyl iodide (*Clous*, Ber. **19**, 2785). Aqueous potash removes the heaviest alkyl group from these ammonium iodides. Alkyl anilines with a tertiary alkyl group have been prepared by *Hickinbottom*, J. **1933**, 946.

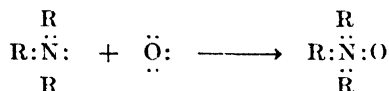
**Methyl-allyl-aniline**, b.p.  $214$ – $216^{\circ}$ , is obtained from methylaniline and allyl bromide. It gives an aniline oxide when oxidised with hydrogen peroxide or permonosulphuric acid. Picrate, m.p.  $121^{\circ}$ . On further treatment with caustic soda the oxide, rearranges to *N*-methyl-O-allyl-N-phenylhydroxylamine, b.p. ( $14$ – $16$  mm.)  $97^{\circ}$  (*Meisenheimer*, Ber. **52**, 1667).

**PHENYLALKYLAMMONIUM BASES.** Tertiary dialkylanilines, such as diethylaniline, combine with alkyl halides to form ammonium compounds. The free bases are liberated by the action of moist silver oxide or lime; triethylphenylammonium iodide,  $\text{PhNEt}_3\text{I}$  gives the hydroxide  $\text{PhNEt}_3\text{OH}$ . By boiling with sodium ethoxide the quaternary salts are smoothly reconverted into tertiary amines (*Vorländer*, Ber. **52**, 309). In substituted anilines with substituents in the ortho-position to the amino-group the formation of quaternary ammonium bases is more difficult or impossible (*Fischer*, Ber. **33**, 345). Similar cases of steric hindrance by ortho-substituents have been mentioned elsewhere (see p. 68). A number of phenylalkyl-ammonium bases have been resolved into optical anti-mers by fractional crystallisation of their bromo-camphor sulphonates (*Thomas*, J. **99**, 280). In solution, especially in solvents containing hydroxyl, these optically

active nitrogen compounds show a strong tendency to autoracemisation, and gradually lose their optical activity.

**DIALKYL ANILINE OXIDES.** These are obtained by oxidising dialkylanilines with hydrogen peroxide or permonosulphuric acid (*Bamberger*, Ber. 39, 4285; *Jones*, Am. 46, 1840). They correspond to trimethylamine oxide,  $\text{Me}_3\text{NO}$  (Vol. I, p. 205), and to the alkyl-piperidine oxides. Dimethylaniline oxide has also been obtained from nitrobenzene by reduction with zinc powder and ammonium chloride in the presence of dimethyl sulphate (*Bamberger*, Ber. 52, 1107). With methyl groups in the *o*-position the formation of dialkylaniline oxides is difficult. With acids they form salts by addition, such as dimethylphenylhydroxyammonium chloride ( $\text{PhNMe}_2\text{OH})\text{Cl}$ . They readily lose oxygen and are therefore oxidising agents. When dimethylaniline oxide is warmed with conc. sulphuric acid, *o*- and *p*-dimethylamino-phenols are the main products. Nitrous acid and sulphur dioxide first form addition products and these immediately rearrange to give nuclear substitution products, viz., nitro-dimethylaniline and dimethylaniline-sulphonic acid (*Bamberger*, Ber. 32, 243, 1882; 34, 12; 39, 4285). Some bromo- and nitro-dimethylaniline oxides unite with methyl iodide to form organic ammonium iodides and periodides (*Brown*, Am. 46, 1836).

Meisenheimer succeeded in resolving methylethylaniline oxide,  $\text{PhMeEtNO}$ , and other amino oxides with three different radicals attached to nitrogen into dextro- and laevo-rotatory forms, with the aid of bromo-camphorsulphonic acid or *d*-tartaric acid (Ann. 385, 117; 499, 188; Ber. 41, 3966). The fact that the amino oxides as well as their hydrates can be resolved into optical antimers proves that in the latter the two hydroxyls are linked in different ways ( $\text{R}_1\text{R}_2\text{R}_3\text{NOH})\text{OH}$ , and that in the former there is a coordinate (*Sudgwick*) or semipolar link between O and N, as is shown by the following formula, in which dots represent electrons:

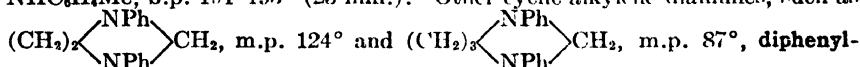


**Methylethylaniline oxide**,  $\text{PhMeEtNO}$ , obtained from methylethylaniline and hydrogen peroxide, forms colourless prisms, and is very hygroscopic. Hydrochloride, m.p.  $124^\circ$ , picrate, m.p.  $148^\circ$ . For its resolution, see above.

**Dimethylaniline oxide**,  $\text{PhNMe}_2\text{O}$ , m.p.  $153^\circ$ , picrate, m.p.  $135^\circ$ , hydrochloride m.p.  $125^\circ$ .

**ALKYLENE MONO- and DI-ANILINES** are obtained by the action of dibromo-paraffins on anilines. The 1,4-dibromides form cyclic alkylene-imines, pyrrolidines (Vol. I, p. 386), unless there is a substituent in the ortho-position to  $\text{NH}_2$ , when steric hindrance comes into play; see above and *Scholtz*, Ber. 32, 848, 2251.

**N-Phenylethylene-diamine**,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHPh}$ , b.p.  $263^\circ$ , is obtained from potassium phthalimide and ethylene dibromide (*Newman*, Ber. 24, 2191). **N,N'-Diphenyl-ethylene-diamine**,  $\text{PhNH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHPh}$ , m.p.  $65^\circ$ . **N,N'-Diphenyl-trimethylene-diamine**,  $\text{PhNH}(\text{CH}_2)_3\cdot\text{NHPh}$ , b.p.  $280\text{--}285^\circ$  (16 mm.), is obtained, together with N-phenyl-trimethyleimine, from trimethylene bromide and aniline. **1,4-Pentylene-di-o-toluidine**,  $\text{MeC}_6\text{H}_4\text{NH}\cdot(\text{CH}_2)_5\text{CH}(\text{Me})\text{NHC}_6\text{H}_4\text{Me}$ , b.p.  $191\text{--}193^\circ$  (23 mm.). Other cyclic alkylene-dianilines, such as



**hydroglyoxaline** and **-pyrimidine**, have been obtained from alkylene-dianilines by the action of aldehydes (*Schultz*, loc. cit.; *Bischoff*, Ber. 31, 3284). **Diethylene-diphenyldiamine**, diphenyl-piperazine, see piperazines (Vol. IV).

**ALKYLIDENE DIANILINES** are readily obtained from an aliphatic aldehyde (one mol.) and an aniline (2 mols.) in cold aqueous solution. They are hydrolysed to their components by mineral acids. Methylene-dianilines, on heating with conc. HCl or aniline hydrochlorides, undergo rearrangement to diaminodiphenylmethanes (*Meyer*, Ber. 33, 250; *Braun*, Ber. 41, 2145). The simpler alkylidene-dianilines readily go over into alkylidene-monoanilines and derivatives of these (see below; *Eifner*, Ann. 302, 335; *Bischoff*, Ber. 36, 41).

**Methylene-dianiline**,  $\text{CH}_2(\text{NHPh})_2$ , m.p.  $65^\circ$ , b.p.  $160^\circ$  (12 mm.), on oxidation with permonosulphuric acid gives diphenylhydroxy-formamidine and various

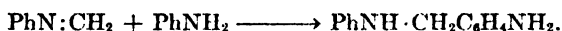
degradation products (p. 90 and *Bamberger*, Ber. 35, 714). **Methylene-*o,o'*- and *p,p'*-ditolylamines**, m.p. 52° and 89°. **Ethylidene-dianiline**,  $\text{CH}_3\text{CH}(\text{NPh})_2$ , m.p. 51°. **Trichloroethylidene-dianiline**,  $\text{CCl}_3\text{CH}(\text{NPh})_2$ , m.p. 107°.

**ALKYLIDENE MONOANILINES** are readily formed by the condensation of equimolecular amounts of aliphatic aldehydes and anilines, water being eliminated. The simple compounds are usually unstable oils, which either polymerise at once (as *e.g.*, formaldehyde-aniline) or undergo an aldol condensation. The alkylidene anilines react with sulphur dioxide and sodium bisulphite in just the same way as aldehydes, although the reaction is not so simple with the derivatives of the

higher aldehydes; ethylidene-aniline gives  $\text{CH}_3\text{CH} \begin{matrix} \swarrow \text{NPh} \\ \searrow \text{SO}_3\text{H} \end{matrix}$ , the sodium salt

of which is also obtained by the addition of aniline to acetaldehyde sodium bisulphite. The simple, as well as the polymeric alkylidene-anilines, readily add on hydrocyanic acid, nitriles or  $\alpha$ -anilido-carboxylic acids being formed. These can also be obtained by the action of potassium cyanide on the bisulphite addition products, and by the action of anilines on aldehyde cyanhydrins, or by the direct action of aniline salts on aldehydes and potassium cyanide (*Knoevenagel*, Ber. 37, 4073; *Bucherer*, Ber. 39, 986, 2796). The condensation products of aldol type, however, do not add on hydrocyanic acid but behave as di-acid dissecondary bases, and add on bromine. They should, therefore, probably be regarded as di-anilido-derivatives of olefine glycols, isomeric with aldols, *e.g.*,  $\text{CH}_3\text{CH}(\text{NPh})\text{CH}(\text{NPh})\text{CH}_2$  or  $\text{CH}_3\text{CH}(\text{NPh})\text{CH}_2\text{CH}(\text{NPh})$ . These substances readily undergo further condensation to quinoline derivatives, with loss of aniline and hydrogen (*Miller*, Ber. 25, 2020; *Eibner*, Ann. 316, 89; 318, 58; *Bucherer*, C. 1902, I, 911).

**Anhydroformaldehyde-aniline**,  $(\text{CH}_2\text{NPh})_n$ , m.p. 140°, is obtained by mixing aqueous formaldehyde with aniline and cooling. It gives methylaniline on reduction, and combines with hydrocyanic acid to give anilido-acetonitrile. The anhydroformaldehyde-anilines condense with aromatic amines in presence of their hydrochlorides, to give aminobenzylanilines:



A condensation product of aniline and formaldehyde, probably heterocyclic, has been described by *Nastjukov*.

**Ethylidene-aniline**,  $\text{CH}_3\text{CH}(\text{NPh})$ , is an oil. It readily adds on hydrocyanic acid to give  $\alpha$ -anilido-propionitrile, and condenses to  $\beta$ -anilido-butylidene-aniline,  $\text{CH}_3\text{CH}(\text{NPh})\cdot\text{CH}:\text{CHNPh}$  of which two stereo-isomeric forms are known with m.p. 126° and 85°, respectively. The lower melting form can easily be converted into the other. Both give quinaldine when heated with HCl or acetic acid. With nitrous acid, two dinitroso-compounds are obtained, m.p. 161° and 120° (see above); the anilino-group in the terminal position is easily detached, whereas the central anilino-group is more firmly bound. **Aldol-aniline**,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}:\text{NPh}$ , obtained from aldol and aniline, is a reddish, unstable oil. With ammonium sulphide it gives **thioaldol-aniline**,  $\text{CH}_3\cdot\text{CH}(\text{OH})\text{CH}_2\text{CH}-\text{NPh}$ , m.p.

92° (*Miller*, Ber. 29, 59). For the higher homologous alkylidene- and aldol-anilines see *Eibner*, Ber. 33, 3460; *Simonis*, Ber. 34, 509; *Friedjung*, Mo. 22, 460. For the course of the catalytic hydrogenation of alkylidene-anilines, see *Mailhe*, Bull. 25, 321.

### 3. Polyphenylamines

The methods of formation and the reactions of these compounds can be illustrated by considering the di- and triphenylamines.

**DIPHENYLAMINE**,  $\text{NH}(\text{C}_6\text{H}_5)_2$ , m.p. 53°, b.p. 310°. 1. This compound, which is important in the aniline dye industry, was discovered by *A. W. Hofmann* in 1864 (Ann. 132, 160). He obtained it by heating *aniline blue*, *rosaniline*, and similar dyes. 2. It is

manufactured commercially in large quantities by heating aniline with aniline hydrochloride at 140°:



Homologues, such as *ditolylamine*, have been obtained by a similar method. 3. Diphenylamine is formed in good yield when aniline is heated with bromobenzene in the presence of copper powder or cuprous iodide. It is best to start with acetanilide, and to prepare first the acetyl compound, from which the free base can be readily liberated. 4. Aryl-anthranilic acids lose  $\text{CO}_2$  when heated under pressure (*Ullmann*, *Ann.* **355**, 312). The last two methods are suitable for preparing asymmetrical and substituted diphenylamines (*Goldberg*, *Ber.* **40**, 4541).

5. Diphenylamine is formed when aniline and phenol are heated with zinc chloride at 260°; and 6. similarly from phospham,  $\text{PN}_2\text{H}$ , by heating with phenol at 200–250° (*J. pr.* **48**, 454). 7. It is also formed when bromobenzene and aniline are heated with soda-lime at 350–390°.

Diphenylamine is a crystalline substance with a pleasant smell. It is almost insoluble in water, but dissolves freely in alcohol and ether. It is a very weak base, and its salts are hydrolysed by water. The hydrogen of the NH group can be replaced by metals, *e.g.*, in the formation of potassium diphenylamine,  $\text{Ph}_2\text{NK}$ .

When diphenylamine is oxidised with  $\text{KMnO}_4$  or  $\text{PbO}_2$  in acetone or benzene solution, *tetraphenyl-hydrazine*,  $\text{Ph}_2\text{N} \cdot \text{NPh}_2$  (p. 149; *Wieland*, *Ber.* **39**, 1500) is formed. In alkaline solution  $\text{KMnO}_4$  oxidises it to *diphenyl-p-azophenylene*, or *quinone-diamil*  $\text{PhN}=\text{N}[\text{C}_6\text{H}_4]_4=\text{NPh}$  (*Baudrowski*, *Ber.* **20**, R 718). Chlorine and bromine convert it into tetra- and hexa-halogen substitution products, and nitric acid into the hexanitro-compound (p. 104). Diphenylamine dissolves in sulphuric acid; traces of nitric acid give an intense blue colour with this solution, and this forms the basis of the well-known test for nitric acid. The blue substance is a holoquinoid oxidation product of  $\text{N,N}'$ -diphenylbenzidine (p. 498), *i.e.*, a diphenoquinone-anil salt (*Kehrmann*, *Ber.* **45**, 2641; *Wieland*, *Ber.* **46**, 3296).

On heating with sulphur, diphenylamine gives thioldiphenylamine,  $\text{NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{S}$ , (Vol. IV), the parent substance of the *thionine dyes*, and with aliphatic acids at 300° it gives *acridines* such as  $\text{N} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CH}$ . Diphenylamine is used in the manufacture of *triphenyl-rosaniline* or *aniline blue* (p. 538).

**Methyl-diphenylamine**,  $\text{MeNHPH}_2$ , b.p. 292° (*Brühl*, *Ann.* **235**, 21; *Gibson*, *J.* **123**, 831).

**Phenyl-p-toluidine**,  $\text{PhNHC}_6\text{H}_4\text{Me}$ , m.p. 87°, and **phenyl-m-xylidine**,  $\text{PhNHC}_6\text{H}_3\text{Me}_2$ , m.p. 43°, are obtained by methods 3 and 4 (above).

**Triphenylamine**,  $(\text{C}_6\text{H}_5)_3\text{N}$ , m.p. 127°, distils without decomp. It is obtained by heating dipotassium aniline or sodium diphenylamine with bromobenzene, best in the presence of catalysts (*Heydrick*, *Ber.* **18**, 2156; *Ger. Pat.* 301,450). The best methods of preparation are by heating diphenylamine with phenyl iodide and a little copper powder (*Huger*, *Org. Synth.* **8**, 116), or by eliminating  $\text{CO}_2$  from diphenylanthranilic acid (*Goldberg*, *Ber.* **40**, 2448; *Wieland*,

Ber. 52, 898). It crystallises from ether in large plates. It dissolves in warm sulphuric acid with an intensely blue colour. It cannot form salts with acids. On nitration it gives a trinitro-derivative which can be reduced to *triamino-triphenylamine* (Heydrick, Ber. 19, 759). By the action of carbonyl chloride *hexaphenyl-rosaniline* is formed.

Triphenylamine is capable of giving up an electron to oxidising agents, thus becoming a cation, which forms salts such as  $\text{Ph}_3\text{N}^+\text{ClO}_4^-$ . Compounds of this kind will be discussed in connection with free radicals (Vol. IV).

*p*-Tritolylamine,  $(\text{MeC}_6\text{H}_4)_3\text{N}$ , m.p.  $117^\circ$ , is obtained from *p*-ditolylamine and *p*-iodotoluene. It forms unstable, dark-blue addition products with  $\text{Br}_2$ ,  $\text{PCl}_5$ ,  $\text{SbCl}_5$ , etc., from which water regenerates tritolylamine (Wieland, Ber. 40, 4263).

Triphenylmethyl-diphenylamine,  $\text{Ph}_3\text{CNPh}_2$ , is obtained from triphenylmethyl and tetraphenyl-hydrazine ("diphenyl-nitrogen") (Vol. IV). It is a colourless substance, melting at  $172^\circ$  to a red liquid. It hydrolyses to triphenyl-carbinol and diphenylamine. Triphenylmethyl-di-*p*-tolylamine, m.p.  $164^\circ$ .

### Aniline Derivatives of Inorganic Acids

**AROMATIC THIONYLAMINES.** These compounds correspond to the alkyl-thionylamines (Vol. I, p. 200), and are obtained by the action of thionyl chloride on primary bases, a reaction characteristic of the latter (Michaelis, Ann. 274, 201; 310, 137). The thionyl-anilines are usually yellow liquids, which boil without decomp. even at ordinary pressure, and have a peculiar smell which is both aromatic and reminiscent of sulphur chloride. See Gilman, Am. 48, 2339; 51, 2252 for their reaction with  $\text{PhMgBr}$ . Thionyl-aniline,  $\text{PhN}:\text{SO}$ , b.p.  $200^\circ$ ,  $d_{15} 1.236$ , reacts with  $\text{PhMgBr}$  to give benzene-sulphonic anilide (p. 181). Thionyl-*o*-chloroaniline, b.p.  $207^\circ$  (46 mm.); *m*-compound, b.p.  $233^\circ$ ; *p*-compound, m.p.  $36^\circ$ , b.p.  $237^\circ$ . Thionyl-*o*-bromoaniline, b.p.  $210^\circ$  (46 mm.); *m*-compound m.p.  $32^\circ$ ; *p*-compound, m.p.  $60^\circ$ . Thionyl-*p*-nitraniline, m.p.  $32^\circ$ .

THIONYL-TOLUIDINES, *o*-, b.p.  $184^\circ$  (100 mm.); *m*-, b.p.  $220^\circ$ ; *p*-, m.p.  $7^\circ$ , b.p.  $224^\circ$  (Michaelis, Ann. 274, 201). For the action of thionyl chloride on tertiary anilines see Michaelis, Ann. 310, 137. For di-*o*-substituted aromatic thionylamines, see Anschutz, Ann. 493, 425.

Phenyl-sulphamic acid,  $\text{PhNHSO}_3\text{H}$ , m.p.  $77-78^\circ$  (Wohl, Ber. 43, 3295), is obtained: 1. By the action of sulphur trioxide or chlorosulphonic acid on aniline in chloroform solution (Traube, Ber. 24, 360). 2. By heating aniline with an amino-sulphonic acid (Paal, Ber. 27, 1214). 3. By the combination of *N*-phenyl-hydroxylamine with sulphur dioxide. 4. By the action of aqueous sodium bisulphite or hydrosulphite on nitrobenzene (Seyewitz, C.r. 142, 1052; Weil, Ber. 55, 732; Ger. Pat. 151,134):



Sulphonic acids are formed as by-products. Phenyl-sulphamic acid is readily decomposed by dilute acids, salts of aniline being formed, while concentrated acids bring about a rearrangement into *o*- (or *p*-) anilinesulphonic acid (Bamberger, Ber. 30, 2274). *p*-Tolyl-sulphamic acid is precipitated from the solution of its ammonium salt by acids (Paal, Ber. 28, 3161). *p*-Chlorophenyl-sulphamic acid,  $\text{ClC}_6\text{H}_4\cdot\text{NHSO}_3\text{H}$ , rearranges to *p*-chloroaniline-*o*-sulphonic acid when heated (Paal, Ber. 34, 2748). For the formation of phenyl-sulphamic acids from anilines and sulphur dioxide see Junghahn, C. 1898, II, 195. Sulphanilide,  $\text{SO}_2(\text{NHPh})_2$ , m.p.  $112^\circ$  (Traube, Ber. 24, 362; Wohl, Ber. 43, 3295).

The aromatic nitrosamines and nitramines will be dealt with later (pp. 110, 111).

**PHOSPHOPHENYLAMINES.** Phosphazobenzene chloride,  $(\text{PhN}:\text{P})\text{Cl}_2$ , m.p.  $136-137^\circ$ , is obtained by the action of  $\text{PCl}_5$  on aniline hydrochloride. It gives: with phenol, phenoxyphosphazobenzene,  $(\text{PhN}:\text{POPh})_2$ , m.p.  $189-190^\circ$ ; and with aniline, phosphazobenzene anilide,  $(\text{PhN}:\text{P}:\text{NHPh})_2$  (Michaelis, Ber. 27, 490; Ann. 326, 147). Anilido-phosphoric dichloride,  $\text{PhNH}\cdot\text{POCl}_2$ , m.p.  $84^\circ$ , is obtained from aniline hydrochloride and  $\text{POCl}_3$ . Orthophosphoric anilide,  $(\text{PhNH})_2\text{PO}$ , m.p.  $208^\circ$  (Michaelis, Ann. 229, 334). Oxyphosphazobenzene

**anilide**,  $\text{PhNH}\cdot\text{PO:NPh}$ , m.p.  $225-226^\circ$ , is obtained by the action of  $\text{POCl}_3$  on aniline, by treating the phosphoryl chloride dianilide first formed with silver oxide. It forms a polymer, m.p.  $357^\circ$  (*Caven*, J. 83, 1045). **Trichloro-phosphanil**,  $\text{PhN:PCl}_3$  is formed from aniline hydrochloride and  $\text{PCl}_5$  (*Gilpin*, Am. Ch. J. 27, 444; *Michaëlis*, Ber. 28, 2212; Ann. 326, 147).

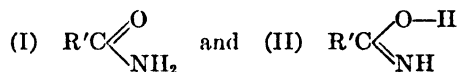
**Thiophosphazobenzene chloride**,  $(\text{PhN:PSCl})_2$ , m.p.  $149^\circ$ , b.p.  $280-290^\circ$ , is obtained from  $\text{PSCl}_3$  and aniline hydrochloride (*Michaëlis*, Ann. 407, 291).

**Arsenophenylamines** are obtained by the action of arsenic trichloride or tribromide on aniline in ether or chloroform. **Arsenanilido-dichloride**,  $\text{PhNHAsCl}_2$ , m.p.  $87^\circ$ . **Arsenanilido-dibromide**, m.p.  $112^\circ$ . **Arsendianilido-monochloride**,  $(\text{PhNH})_2\text{AsCl}$ , m.p.  $127^\circ$ . **Arsenanilido-dimethyl ether**,  $\text{PhNHAs(OMe)}_2$ , b.p.  $55^\circ$  (12 mm.) (*Anschütz*, Ann. 261, 279).

**Silico-tetraphenylamide**,  $\text{Si(NHPh)}_4$ , is converted into **silico-diphenylimide**,  $\text{Si(NPh)}_2$ , on heating (*Reynolds*, J. 83, 252).

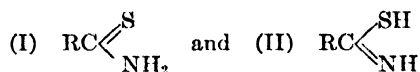
### *Derivatives of Primary and Secondary Amines with Carboxylic Acids*

The methods by which nitrogenous derivatives can be obtained by substitution in the carboxyl group, and the classification of such derivatives, have been dealt with in connection with the fatty acids, taking acetic acid as an example (Vol. I, p. 279). The amides of carboxylic acids comprise the first class of these compounds. They can be represented by the following two formulae:



The imido-ethers are derived from formula II. Many fatty acid derivatives of this type have been obtained with aniline and its primary homologues. The acid amides of secondary bases can only have formula I. In a primary amine both hydrogen atoms can be replaced by acid radicals; the introduction of a second acyl-group is facilitated by the presence of *o*-substituents in the aniline nucleus. The presence of such groups, however, retards the entry of the first acyl-group (*Sudborough*, Proc. 1901, 45).

The *thio-amides*, and *isothio-amides*:



are analogous to the *acid amides*. *Amido-chlorides*, *imido-chlorides*, and *amidines*, also fall into this class of compounds.

**ANILIDES OF MONOBASIC FATTY ACIDS.** The anilides, or phenylamides, are obtained by similar methods to those used for the simple amides (Vol. I, p. 321): 1. By heating the aniline salts of fatty acids. 2. By the action of aniline on esters, or 3. on acid chlorides, or 4. on acid anhydrides. 5. They are also formed by the action of esters on  $\text{PhNHMgI}$  (*Bodroux*, C.r. 138, 1427).

The anilides are very stable, and most of them can be distilled without decomposition. They can be directly chlorinated, brominated, and nitrated (p. 102). They provide a simple and rapid method of characterising the aromatic bases. When warmed with alkalis or heated with hydrochloric acid, they are decomposed into their components. When boiled with sulphur they give benzthiazoles.



Secondary anilides react with nitrous acid in the same way as the secondary alkyl-anilines (p. 80), *nitroso-anilides* being formed. These give the nitrosamine reaction when treated with phenol and sulphuric acid, but are not so stable as the nitrosamines of secondary anilines. The nitroso-group is removed by reducing agents. The hydrogen of the NH group in anilides can be replaced by halogen by means of sodium hypochlorite or hypobromite,  $\text{Ph}\cdot\text{NCl}\cdot\text{COCH}_3$ , for example, being formed. These N-halides readily rearrange to anilines substituted in the nucleus, especially under the influence of HCl or in sunlight: thus,  $\text{PhN}\cdot\text{Cl}\cdot\text{COCH}_3 \rightarrow \text{Cl}[4]\text{C}_6\text{H}_4\text{NHCOCCH}_3$  (*Chattaway*, Ber. 32, 3573; Proc. 1902, 200; *Blanksma*, Rec. 21, 366; *Orton et al.*, J. 1927, 986; 1928, 998; 1929, 2810).

**Formanilide**,  $\text{Ph}\cdot\text{NH}\cdot\text{CHO}$ , m.p.  $40^\circ$ , b.p.  $284^\circ$  (*Nef*, Ann. 270, 279), is obtained by boiling aniline with formic acid, or by heating it rapidly with oxalic acid. It is soluble in water, alcohol, and ether.

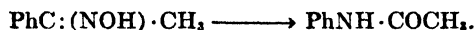
**SALTS AND ALKYL DERIVATIVES.** Sodium formanilide,  $\text{PhN}:\text{CHONa}$ , is a crystalline precipitate formed by adding sodium hydroxide to an aqueous solution of formanilide. With methyl iodide it gives methyl-formanilide,

$\text{PhN} \begin{cases} \text{CHO} \\ \text{CH}_3 \end{cases}$ , m.p.  $12.5^\circ$ , b.p.  $253^\circ$ . When this is warmed with alcoholic potash

or HCl it is decomposed to methyl-aniline and formic acid (*Pictet*, Ber. 21, 1107).

**Silver formanilide**,  $\text{PhN}:\text{CH}(\text{OAg})$ , is precipitated when silver nitrate is added to the alcoholic solution of the sodio-compound. With methyl iodide it gives methyl isoformanilide,  $\text{PhN}:\text{CHOMe}$ , b.p.  $196^\circ$ , which is converted on heating into the isomeric methyl-formanilide (*Comstock*, Am. Chem. J. 12, 493; cf. Ber. 23, 2274; *Wislicenus*, Ber. 33, 1470). On the other hand, with acid chlorides, such as benzoyl chloride, the silver compound gives N-derivatives (*Wheeler*, Am. Chem. J. 18, 381). **Ethyl-isoformanilide**, *ethoxymethylene aniline*,  $\text{PhN}:\text{CHOEt}$ , is also obtained, together with diphenyl-formamidine, by prolonged boiling of aniline with orthoformic ester. It boils at  $212^\circ$  (*Claisen*, Ann. 287, 360).

**Acetanilide**, *antifebrin*,  $\text{PhNHCOCCH}_3$ , m.p.  $114^\circ$ , b.p.  $295^\circ$ , is formed when aniline is boiled with glacial acetic acid (*Meyer*, Ber. 15, 1977; for rate of reaction see *Menschutkin*, J. pr. 26, 208). It is also obtained from aniline by the action of acetyl chloride, acetic anhydride, or thioacetic acid. The last-named reagent has been found to be very suitable for the introduction of acetyl groups into anilines (*Pawlewski*, Ber. 35, 110). Acetanilide is also obtained from malonanilic acid by loss of  $\text{CO}_2$ . Its formation from the isomeric acetophenone oxime by treatment with sulphuric acid at  $100^\circ$  is noteworthy (*Beckmann transformation*; Ber. 20, 2581):



Acetanilide crystallises from water, in which it is sparingly soluble in the cold, in small white leaflets. It is used as an antipyretic, and in the treatment of rheumatism. For the action of  $\text{PCl}_5$ , see *Wallach*, Ann. 184, 86. When heated with sulphur it gives benz-thiazole. **Bromoacetanilide**, m.p.  $131^\circ$ , when fused in air with caustic potash, gives *indigo*.

**SALTS.** The hydrochloride is decomposed by water. On heating it gives diphenylacetamidine, flavaniline, and dimethyl-quinoline (*Noelting*, Ber. 18, 1340). When heated with sodium ethoxide it gives ethyl-aniline and sodium acetate (*Baubigny*, C.r. 109, 149).

**Sodium acetanilide**,  $\text{PhN}:\text{C}(\text{ONa})\text{CH}_3$ , is obtained by the action of sodium on acetanilide in xylene solution. It gives monoalkyl-acetanilides with alkyl iodides (*Hepp*, Ber. 10, 328), from which monoalkyl-anilines can be obtained (*Paal*, Ber. 23, 2587). These same alkyl-acetanilides are obtained by the action of acetic anhydride on the secondary bases. On the other hand when acetanilide is acted upon by silver oxide and methyl iodide, or when it is heated with dimethyl sul-

phate, aceto-phenylimido-methyl ether, b.p. 197° is formed (Lander, J. 79, 690). Mercuric acetanilide,  $(\text{PhNCOCH}_3)_2\text{Hg}$  (Piccinini, Gazz. 24, II, 453).

**Methyl-acetanilide**, *exalgin*, m.p. 101°, b.p. 253°, is an antineuralgic. **Ethyl-acetanilide**, m.p. 54°, b.p. 258°. **n-Propyl-acetanilide**, m.p. 47°, b.p. 266° (Pictet, Ber. 21, 1108).

**SUBSTITUTED ACETANILIDES.** *o*- and *p*-Derivatives are obtained when acetanilide is acted upon by chlorine, bromine, or nitric acid (p. 101).

**Formyl-acetanilide**,  $\text{PhN}(\text{COH})\text{COCH}_3$ , m.p. 56°, is obtained from mercuri-formanilide and acetyl chloride (Wheeler, Am. Chem. J. 18, 659).

**Diacetanilide**,  $\text{PhN}(\text{COCH}_3)_2$ , m.p. 37°, b.p. 142° (11 mm.), is formed when acetanilide is heated with acetyl chloride at 170-180°, or with acetic anhydride (Young, J. 1896/7, 156), or directly from aniline by the action of an excess of acetic anhydride, or by boiling phenyl mustard oil with acetic anhydride (Bistrzycki, Ber. 27, 91; Clayton, *ibid.* 28, 1665). Its physiological effects are similar to those of acetanilide (Bistrzycki, Ber. 31, 2788). Diacetanilide isomerises to *p*-acetaminoacetophenone,  $(\text{CH}_3\text{CO})_2\text{NPh} \rightarrow \text{CH}_3\text{CONHC}_6\text{H}_4\text{COCH}_3$  (Chattaway, Proc. 1902, 173; 1903, 124).

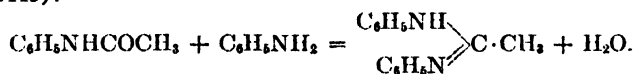
The acetyl-compounds crystallise readily, and are useful for characterising many primary and secondary aromatic bases. Their melting points have therefore been given together with those of the bases on pp. 78 and 79.

**THIOANILIDES** are obtained by the action of  $\text{P}_2\text{S}_5$  on anilides, by the action of  $\text{H}_2\text{S}$  on amidines and isonitriles, and by the action of magnesium alkyl iodides on phenyl mustard oil. **Thioformanilide**,  $\text{PhNHCSH}$ , melts at 137° with decomposition into  $\text{H}_2\text{S}$  and phenyl isocyanide (Hofmann, Ber. 11, 338; Bernthsen, Ann. 192, 45). For homologous thioformanilides see Senier, Ber. 18, 2292.

**Thioacetanilide**, m.p. 75°, is oxidised by potassium ferricyanide to methyl-benzthiazole,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{N} \diagdown \\ \diagdown \text{S} \diagup \end{smallmatrix} \text{C} \cdot \text{CH}_3$ ; thioanilides of homologous fatty acids are also known (Sachs, Ber. 36, 587). **N-Methylthioacetanilide**, m.p. 59°, b.p. 290°.

**Methyl-isothioacetanilide**,  $\text{PhN} : \text{C} \begin{smallmatrix} \diagup \text{CH}_3 \\ \diagdown \text{SCH}_3 \end{smallmatrix}$ , b.p. 245°, and **ethyl-isothioacetanilide**, b.p. 250°, are obtained by the action of sodium ethoxide and methyl or ethyl iodide on thioacetanilide (*cf.* phenyl-isothio-urethanes and phenyl-isothio-ureas, p. 95). When they are shaken with  $\text{HCl}$  they decompose, giving aniline hydrochloride and ethyl thioacetate (Vol. I, p. 320) (Wallach, Ber. 12, 1061).

**PHENYLATED AMIDINES OF FORMIC AND ACETIC ACIDS.** In addition to the general methods of preparation of the amidines given in Vol. I, the phenylated amidines are obtained by the action of  $\text{PCl}_5$  or  $\text{HCl}$  on a mixture of aniline and an anilide, water being eliminated (Wallach, Ber. 15, 208; Tobias, Ber. 15, 2449):



They are weak bases which combine with one equivalent of  $\text{HCl}$  to form salts. When boiled with alcohol they decompose into aniline and anilides.

**Diphenyl-formamidine**,  $\text{PhN} : \text{CH} \cdot \text{NHPh}$ , m.p. 135°, has also been obtained by heating aniline with chloroform, or formic acid at 180°, by the action of aniline on hydrogen cyanide sesquihydrochloride,  $(\text{HCN})_2(\text{HCl})_3$  (Dains, Ber. 35, 2498), and by boiling phenyl isocyanide,  $\text{PhCN}$ , with aniline. It crystallises from alcohol in long needles and distils at about 250°, with partial decomposition into benzonitrile and aniline.

The diaryl-formamidines are more reactive than those of higher carboxylic acids. Diphenyl-formamidine, for example, reacts with the  $\text{CH}_2$ -group of malonic ester, aceto-acetic ester, and similar substances, with the formation of aniline and anilino-methylene derivatives, such as *anilino-methylene-malonic ester*,  $\text{PhNHCH} : \text{C}(\text{CO}_2\text{R})_2$ , *anilino-methylene-acetoacetic ester*,  $\text{PhNHCH} : \text{C}(\text{COCH}_3) \cdot \text{CO}_2\text{R}$ , etc. (Diams, Ber. 35, 2505).

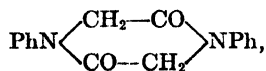
**Diphenyl-hydroxy-formamidine**,  $\text{PhN}:\text{CH}\cdot\text{N}(\text{OH})\text{Ph} + \text{H}_2\text{O}$ , m.p. anhydrous,  $131^\circ$ , is obtained from methyl-isofornanilide (p. 88) by the action of N-phenyl-hydroxylamine, and from methylene-di-phenylhydroxylamine,  $\text{CH}_2(\text{N}(\text{OH})\text{Ph})_2$ , by elimination of water, by the action of anhydrous copper sulphate. In the presence of acetic anhydride it isomerises to *sym*-diphenyl-urea,  $\text{PhNH}\cdot\text{CO}\cdot\text{NHPH}$  (Ley, Ber. 35, 1451; Bamberger, Ber. 35, 1874).

**Diphenyl-acetamidine**,  $\text{PhN}:\text{C}(\text{NHPH})\cdot\text{CH}_3$ , m.p.  $131^\circ$ , is obtained by the action of  $\text{MeMgI}$  on diphenyl-carbodiimide (p. 99). **Phenyl-acetamidine**,  $\text{PhN}:\text{C}(\text{NH}_2)\cdot\text{CH}_3$ , is a liquid obtained from acetonitrile and aniline hydrochloride (Bernthsen, Ann. 184, 362; 192, 25) (Vol. I, p. 327). **Phenyl-isuretine**,  $\text{PhNH}\cdot\text{CH}:\text{NOH}$ , m.p.  $138^\circ$  (decomp.) is obtained from formyl-chloridoxime (Vol. I, p. 289) by the action of aniline (Nef, Ann. 280, 291).

**ARYL ISOCYANIDES.** **Phenyl isocyanide**, **phenyl isonitrile**, **phenyl carbylamine**,  $\text{PhN}\rightarrow\text{C}$ , boils at  $166^\circ$  under atmospheric pressure with rapid polymerisation, but at 20 mm. pressure it boils unchanged at  $64^\circ$ . The liquid,  $d_{16} 0.977$ , is first colourless, but soon turns blue, then dark-blue, and resinifies. It is obtained from aniline and chloroform by the action of alcoholic potash, and by heating thioformanilide (p. 89). Phenyl carbylamine has an intolerable and persistent odour, a bitter taste, and causes headache and flow of saliva. It reacts as follows: 1. At  $220^\circ$  it isomerises to *benzonitrile*,  $\text{PhCN}$ . 2. Nascent hydrogen reduces it to *N-methyl-aniline*. 3. With  $\text{HCl}$  in dry ether it gives *phenyl-imido-formyl-chloride*. 4. With acetic acid it gives *formanilide*. 5. With  $\text{H}_2\text{S}$  at  $100^\circ$  it gives *thioformanilide*,  $\text{PhNH}\cdot\text{CHS}$  (but acetanilide with thioacetic acid, Pawlewski, Ber. 32, 1425). 6. With sulphur at  $130^\circ$  it gives *phenyl mustard oil*,  $\text{PhNCS}$ . 7. With aniline at  $170^\circ$  it gives *diphenyl-formamidine*,  $\text{PhN}:\text{CH}\cdot\text{NHPH}$ . 8. With chlorine it gives *phenylimido-carbonyl chloride*,  $\text{PhN}:\text{CCl}_2$  (p. 98). 9. With carbonyl chloride it gives  $\text{PhN}:\text{CCl}\cdot\text{CO}\cdot\text{CCl}:\text{NPh}$ . 10. With acetyl chloride it gives pyruvic anilide chloride (Nef, Ann. 270, 174). 11. With  $\text{N}_3\text{H}$  it gives *N-phenyl-tetrazole* or *N-phenyl-pyrro- $\alpha,\beta,\beta'$ -triazole* (Gibson, J. 117, 819). *o*-Tolyl isocyanide, b.p.  $75^\circ$  (16 mm.),  $d_{24} 0.968$ . *p*-Tolyl isocyanide, m.p.  $91.6^\circ$ , b.p. (32 mm.)  $99^\circ$  (Smith, Am. Chem. J. 16, 372). *m*- and *p*-Phenylene di-isocyanides rearrange to isophthalic nitrile and terephthalic nitrile on heating (Kaufler, Mo. 22, 1073).

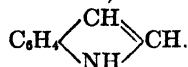
**PHENYLAMINO DERIVATIVES OF CARBOXYLIC ACIDS.** These compounds are capable of some condensation reactions in which the hydrogen of the ring in the ortho-position to nitrogen often participates, heterocyclic compounds being formed. The acids are obtained by heating halogeno-fatty acids with anilines (Bischoff, Ber. 30, 2303, 2464, 3169; 31, 2678), and their nitriles are produced 1. by adding  $\text{HCN}$  to alkylidene anilines; 2. from the bisulphite addition compounds of the latter (p. 83) by the action of  $\text{KCN}$  (Knovenagel, Ber. 37, 4073); 3. by heating aldehyde or ketone cyanohydrins with aniline; 4. by the direct action of aniline salts on aldehydes or ketones and  $\text{KCN}$  (Bucherer, Ber. 39, 986, 2796).

**Anilido-acetic acid**, **phenyl-glycocol**, **phenyl-glycine**,  $\text{PhNHCH}_2\text{CO}_2\text{H}$ , m.p.  $127^\circ$ , is obtained by heating chloro- or bromo-acetic acid with aniline and water (Schwebel, Ber. 18, 2046; Rebuffat, Gazz. 17, 231; U. S. Pat. 1,442,743). Its alkyl esters are obtained by heating an aqueous suspension of aniline with ethyl chloracetate or dichloro-vinyl ether (Ger. Pats. 194,884 and 199,624) or by the action of diazo-acetic ester (Vol. I, p. 458) on aniline. Its nitrile, m.p.  $43^\circ$ , is obtained: 1. from anhydro-formaldehyde-aniline by the action of anhydrous hydrogen cyanide; 2. from the bisulphite compound of the former with  $\text{KCN}$ ; 3. from formaldehyde-cyanohydrin by the action of aniline; 4. from aniline hydrochloride, formaldehyde, and  $\text{KCN}$  (Ger. Pats. 132,621, 138,098 and 151,538).  $\text{N}_2\text{O}_5$  converts it quantitatively into *p*-nitroso-phenylglycine, a brown powder, which explodes on heating (Houben, Ber. 46, 3984). When the free acid is heated to  $150^\circ$ , diphenyl-glycine anhydride, or diphenyl-diketo-piperazine,



m.p.  $263^\circ$ , is formed (Bischoff, Ber. 25, 2270). Phenylglycine is a very important substance in industry because, on fusion with caustic potash, or better with

sodamide, it forms *indoxyl*,  $C_6H_5 \begin{smallmatrix} \diagup C(OH) \\ \diagdown NH \end{smallmatrix} CH$ , which is readily oxidised in air to *indigo*. It is also used as a photographic developer. When calcium anilido-acetate is distilled with calcium formate, *indole* (Vol. IV), is formed:



Besides phenylglycine, aniline and chloroacetic acid form **anilino-diacetic acid**,  $PhN(CH_2CO_2H)_2$ , m.p. 150–155°. On oxidation with  $KMnO_4$  this gives **formyl-phenylglycine**,  $PhN(CHO)CH_2CO_2H$ , m.p. 125°, which, however, is better prepared from phenylglycine by heating with formic acid (*Vorländer*, Ber. 34, 1647). **Anilino-diacetic anhydride**,  $PhN(CH_2CO)_2O$ , m.p. 148°; imide,  $PhN(CH_2CO)_2-NH$ , m.p. 158° (*Bischoff*, Ber. 22, 1809; 25, 2272; *Hausdörfer*, Ber. 22, 1802); phenylimide,  $PhN(CH_2CO)NPh$ , m.p. 152°. **Diglycol-anilic acid**,

$O \begin{smallmatrix} \diagup CH_2CONHPh \\ \diagdown CH_2CO_2H \end{smallmatrix}$  m.p. 118°, is prepared from diglycollic anhydride and aniline;

with acetyl chloride it gives **diglycollic phenylimide**,  $O(CH_2CO)_2NPh$ , m.p. 116°. **Thiodiglycol-anilic acid** and **-anilide** have also been prepared (*Anschutz*, Ann. 273, 66, 70).

**N-Methyl-phenylglycine**,  $PhN(Me)CH_2CO_2H$ , is obtained by heating methyl-aniline with chloroacetic acid. The *nitrile*, b.p. 266° is formed by the action of methylaniline on formaldehyde-cyanohydrin. **Amide**, m.p. 163° (*Warunis*, Ber. 37, 2636).

**Dimethyl-phenyl-betain**,  $PhN^+(Me)_2 \cdot CH_2CO_2^- + H_2O$ , m.p. 124°, is obtained by the action of chloroacetic acid on dimethylaniline. When heated it isomerises to **methyl methyl-phenyl-glycocolate**, b.p. (10 mm.) 141° (*Willstätter*, Ber. 37, 415). **o-Nitro-phenyl-glycine**,  $NO_2[2]C_6H_4[1]NHCH_2CO_2H$ , m.p. 193°; cf. *quinolines*, Vol. IV.

**α-Anilido-propionic acid**, *N-phenyl-alanine*,  $PhNHCH(Me)CO_2H$ , m.p. 162°, is obtained from its nitrile, the product of interaction of acetaldehyde cyanohydrin with aniline, or of ethylidene-aniline with  $HCN$  (*Tiemann*, Ber. 15, 2036; *Nastvogel*, Ber. 23, 2010; *Müller*, Ber. 25, 2032). **α-Anilido-isobutyric acid**,  $PhNHC(Me)_2CO_2H$ , m.p. 185°; nitrile, m.p. 94° (*Bucherer*, Ber. 39, 989). **β-Anilido-propionic ester**, b.p. (18 mm.) 175° is obtained from β-iodo-propionic ester (*Harries*, Ber. 29, 514). **β-Anilido-fatty acids** are also obtained by combining aniline with olefinic-carboxylic acids (*Authenrieth*, Ber. 36, 1262).

**Dianilido-acetic acid**,  $(PhNH)_2CHCO_2H$ , m.p. 88–93°, is obtained by the action of aniline on diacetyl-glyoxylic acid. It readily loses one mol. of aniline to form the anil of glyoxylic acid. Warmed with aniline and aniline hydrochloride it isomerises to *p,p*-diamino-diphenyl-acetic acid (p. 556) (*Ostromisslensky*, Ber. 41, 3031; *Heller*, *ibid.* 4264).

**ANILINE DERIVATIVES OF KETOCARBOXYLIC ACIDS.** **Pyruvic anilide**,  $CH_3COCO \cdot NHPh$ , m.p. 104°. **Pyruvic anilide chloride**,  $CH_3COCOCl \cdot NPh$ , b.p. (13 mm.) 136°, is obtained from phenyl isocyanide (p. 90) by the action of

acetyl chloride (*Nef*, Ann. 270, 299). The anil of pyruvic acid,  $PhN : C \begin{smallmatrix} \diagup CH_3 \\ \diagdown CO_2H \end{smallmatrix}$ ,

m.p. 122° (decomp.) is obtained from aniline and pyruvic acid in ether, and readily goes over into the anil of uvitonic acid, a quinoline derivative (*Böttlinger*, Ann. 263, 126).

**Aceto-acetic anilide**,  $CH_3 \cdot CO \cdot CH_2 \cdot CONHPh$ , m.p. 85°, is obtained from acetoacetic ester and aniline at 130°. It is converted by concentrated sulphuric acid into γ-methylcarbostyryl (Vol. IV). At ordinary temperature aniline and acetoacetic ester unite to form a compound which may be β-phenyl-imino-butyric

ester,  $PhN : C \begin{smallmatrix} \diagup CH_2CO_2Et \\ \diagdown CH_3 \end{smallmatrix}$ , or β-anilido-crotonic ester,  $PhNHC \begin{smallmatrix} \diagup CHCO_2Et \\ \diagdown CH_3 \end{smallmatrix}$ ,

b.p. (16 mm.) 163°. It combines additively with  $HCN$  (*Schroeter*, Ber. 35, 2078), and is decomposed into its components by acids or alkalis. When heated at ordinary pressure it condenses to γ-hydroxy-quinaldine and phenyl-lutidone-

carboxylic acid (Vol. IV). Toly-amino compounds behave similarly (Conrad, Ber. 20, 947; 21, 523; 22, 83; Knorr, Ber. 20, 1398).

**ANILINE DERIVATIVES OF CARBONIC ACID.** The numerous compounds belonging to this class are treated in the same sequence as the amino and alkylamino derivatives of carbonic acid in Vol. I (p. 490).

**Carbanilic acid, phenyl-carbamic acid**, is unknown in the free state. Its salts are obtained by the action of very dilute aqueous caustic alkalis and alkaline earths on phenyl isocyanate (p. 97). On acidification, or even with carbon dioxide, the salts immediately break up into carbon dioxide and aniline (Mohr, J. pr. 73, 177). The esters are known as **phenyl-urethanes**, and are frequently used for characterising alcohols and phenols. They are obtained: 1. from aniline and chloro-carbonic esters; 2. from phenyl isocyanate by the action of alcohols (Hofmann, 1870); 3. from phenyl-carbamyl chloride and alcohols; 4. from benzoyl azides and alcohols (Vol. I, p. 492). The **methyl ester**,  $\text{PhNHCO}_2\text{Me}$ , m.p. 47° forms amino-sulpho-benzoic ester with sulphuric acid. **Ethyl ester**, m.p. 52° (Struve, J. pr. 52, 227; Hofmann, Ber. 3, 654; Hentschel, Ber. 18, 654, 980; Lellmann, Ber. 24, 2108).

**CARBAMYL CHLORIDES** are obtained from secondary aromatic bases by the action of carbonyl chloride in benzene solution, in the presence of pyridine (Meyer, J. pr. 53, 369). **Phenyl-carbamyl chloride**,  $\text{PhNH}\cdot\text{COCl}$ , m.p. 59°, and **bromide**, m.p. 67° (Lengfeld, Am. Chem. J. 17, 98). **Methyl-phenyl-car-**

**bamyl chloride**,  $\begin{matrix} \text{Me} \\ \diagup \\ \text{N}\cdot\text{COCl} \end{matrix}$ , m.p. 88°, b.p. 280°. **Diphenyl-carbamyl chloride**,  $\begin{matrix} \text{Ph} \\ \diagup \\ \text{N}\cdot\text{COCl} \end{matrix}$ , m.p. 85°. With benzene and aluminum chloride these compounds form benzoic amides (cf. the synthesis of aromatic carboxylic acids). With sodium in ether di-*p*-tolyl-urea chloride, m.p. 102°, gives a tetra-substituted oxamide (p. 100) (Lellmann, Ber. 20, 2118; 24, 2108; Kym, Ber. 23, 424; Hammerick, Ber. 25, 1819, 1825).

**PHENYLATED UREAS, PHENYLCARBAMIDES.** **Phenyl-urea**, phenyl-carbamide,  $\text{NH}_2\text{CONHPh}$ , m.p. 144°, is obtained: 1. from cyanic acid and aniline by evaporating a mixed solution of aniline hydrochloride and potassium isocyanate (Weith, Ber. 9, 820); 2. by the action of ammonia on phenylisocyanate (p. 97). By the action of dilute hypochlorous acid one H atom in the  $\text{NH}_2$  group is replaced by Cl; the resulting compound is reduced by hydrochloric acid to phenylurea, and under certain conditions the Cl atom enters the nucleus in the para-position, and *p*-chlorophenyl-urea is formed (Elliot, J. 123, 804).

**sym-Alkyl-phenyl-ureas** are obtained by the action of aniline on isocyanic esters, or by the action of phenyl isocyanate (p. 97) on alkylamines. **sym-Ethyl-phenyl-urea**,  $\text{EtNHCONHPh}$ , m.p. 99°.

**as-Alkyl-phenyl-ureas** are obtained by the action of potassium isocyanate on the hydrochlorides of alkyl-anilines. **as-Ethyl-phenyl-urea**, m.p. 62°.

**sym-Diphenyl-urea**, carbaniide,  $\text{CO}(\text{NHPh})_2$ , m.p. 235°, b.p. 260° is obtained: 1. by the action of carbonyl chloride on aniline (Hentschel, Ber. 16, 2301); 2. by the action of phenyl isocyanate on aniline (A. W. Hofmann, Ann. 74, 15); 3. from *sym*-diphenyl-thiourea by the action of  $\text{HgO}$  or alcoholic potash (A. W. Hofmann, Ann. 70, 148); 4. by heating aniline and urea to 170°, or from 2 mols. aniline and 1 mol. urea in acetic acid (Sonn, Ber. 47, 2437); 5. from monophenyl-urea and aniline at 190° (Weith, Ber. 9, 820); 6. from diphenyl carbonate and aniline at 170° (Eckenrodt, Ber. 18, 516); 7. by heating oxanilide with  $\text{HgO}$  (Taussig, Mo. 25, 375); 8. by the action of water on phenyl isocyanate. Carbaniide forms silky needles freely soluble in alcohol and ether, but sparingly soluble in water.

**as-Diphenyl-urea**,  $\text{NH}_2\text{CONPh}_2$ , m.p. 189°, decomposes slowly when heated giving diphenylamine and cyanic acid. It is obtained from diphenyl-carbamyl chloride and alcoholic ammonia at 100°.

**Triphenyl-urea**,  $\text{PhNH}\cdot\text{CO}\cdot\text{NPh}_2$ , m.p. 132°, and **tetraphenyl-urea**,  $\text{Ph}_2\text{N}\cdot\text{CO}\cdot\text{NPh}_2$ , m.p. 183°, have also been obtained from diphenyl-carbamyl chloride (Steindorff, Ber. 37, 963).

**CYCLIC ALKYLENE-PHENYL-UREA DERIVATIVES** (cf. Vol. I, p. 497):  
**Ethylene-phenyl-urea**, see *Newman*, Ber. 24, 2192. **Trimethylene-phenyl-urea**  
 (*Goldenring*, Ber. 23, 1173). **Ethylene-carbanilide**,  $\text{CO} \begin{array}{l} \diagup \text{N(Ph)-CH}_2 \\ \diagdown \text{N(Ph)-CH}_2 \end{array}$ , m.p.

183°. **Trimethylene-carbanilide**, m.p. 153° (*Hanssen*, Ber. 20, 783).

**UREIDES OF PHENYLATED UREAS** of monocarboxylic acids. **Acetyl-phenyl-urea**,  $\text{CH}_3\text{CONH}\cdot\text{CO}\cdot\text{NHPh}$ , m.p. 183°, is obtained from phenyl-urea by the action of acetic anhydride or acetyl chloride (*M'Creath*, Ber. 8, 1181), or from phenyl isocyanate by the action of aceto-chloramide (*Stieglitz*, Am. Chem. J. 30, 412). **Acetyl-carbanilide**,  $\text{PhNH}\cdot\text{CO}\cdot\text{N}(\text{COCH}_3)\cdot\text{Ph}$ , m.p. 115° (*Kühn*, Ber. 17, 2882).

**UREIDES DERIVED FROM HYDROXY-ACIDS**. **N-Phenyl-hydantoin**, m.p. 194°, is obtained from phenyl-glycine and urea at 160°, or from chloro-acetyl-urethane and aniline (*Fierichs*, Arch. Pharm. 237, 331; for homologues see *Frerichs*, *ibid.* 243, 681). **Phenyl-ethyl-hydantoin**,  $\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{NH} \\ | \\ \text{CO} \cdots \text{C}_2\text{H}_5\text{Ph} \end{array}$ , m.p. 199°, is

obtained from phenylethyl ketone and ammonium cyanide, and subsequent treatment with potassium cyanate and hydrolysis. It is used as a soporific under the name of *nurvanol* (*Read*, Am. 44, 1746). It has been resolved into its enantiomorphs, m.p. 237°,  $[\alpha]_D +122^\circ$  and  $-123^\circ$  (*Sobotka*, Am. 54, 4697). **Diphenyl-hydantoin**, m.p. 139° (*Bischoff*, Ber. 25, 2274).

**PHENYLATED DERIVATIVES OF ISO-UREA** are obtained from phenylated cyanamides (p. 99) by the action of alcohols and HCl, in the same way as imidoethers are obtained from nitriles:

**Methyl-phenyl-isourea**  $\text{PhNHC}(\text{OCH}_3):\text{NH}$ , see *MacKee*, Am. Chem. J. 26, 209.

**Ethyl-phenyl-isourea**  $\text{PhNHC}(\text{OC}_2\text{H}_5):\text{NH}$ , b.p. 138° (19 mm.), *Stieglitz*, Ber. 32, 1494.

**Ethyl-phenyl-methyl-isourea**  $\text{PhNCH}_2\cdot\text{C}(\text{OC}_2\text{H}_5):\text{NH}$ , b.p. 137° (21 mm.), *Stieglitz*, Ber. 33, 807.

**Ethyl-diphenyl-isourea**  $\text{PhN:C}(\text{OC}_2\text{H}_5)\text{NHPh}$ , b.p. 200° (20 mm.), oily.

**Methyl-ditolyl-isourea**, m.p. 48°; b.p. 199° (11 mm.). The last two substances are obtained from diaryl-carbodiimides (p. 99) by the action of alcohol at 180–190°, or, better, by the action of sodium alkylates. They give addition products with HCl. They are readily decomposed by acids, but are quite stable towards alkalis and amines.

**Triphenylchlorocarbamidine**,  $\text{ClC} \begin{array}{l} \diagup \text{NC}_6\text{H}_5 \\ \diagdown \text{N}(\text{C}_6\text{H}_5)_2 \end{array}$ , m.p. 92°, is obtained by the

action of  $\text{PCl}_5$  on triphenylurea. With sodium ethylate it gives ethyl-triphenyl-isourea,  $\text{PhN:C}(\text{OC}_2\text{H}_5)\text{NPh}_2$ , m.p. 49° (*Steindorff*, Ber. 37, 964).

**Phenylated ureas of carbonic acid**. **Ethyl phenyl-allophanate**,  $\text{PhNH}\cdot\text{CO}\cdot\text{NHCO}_2\text{C}_2\text{H}_5$ , m.p. 120° (*Stojentin*, J. pr. [2] 32, 18). **Diphenyl-allophanic acid** (*Hofmann*, Ber. 4, 246). **sym-Phenyl-biuret**,  $\text{PhN}:(\text{CONH}_2)_2$ , m.p. 192°, is obtained by the action of  $\text{PCl}_5$  on phenyl-urea. **as-Phenyl-biuret**,  $\text{PhNH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CONH}_2$ , m.p. 167°. **Diphenyl-biuret**,  $\text{PhNH}\cdot\text{CONH}\cdot\text{CO}\cdot\text{NHPh}$ , m.p. 210°, is obtained by heating phenyl-urea with an excess of  $\text{COCl}_2$ . **Triphenyl-biuret**, m.p. 147° (*Hofmann*, Ber. 4, 250; *Schiff*, Ann. 352, 73).

**PHENYLATED HYDROXYLAMINE AND HYDRAZINE DERIVATIVES OF UREA**. **as-Phenyl-hydroxylurea**,  $\text{PhNH}\cdot\text{CO}\cdot\text{NHOH}$ , m.p. 140° (decomp.), is obtained by the action of hydroxylamine hydrochloride on phenylisocyanate (*Kall*, Ann. 263, 264). **Phenyl-semicarbazide**, *phenylcarbamic hydrazide*,  $\text{PhNH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , m.p. 120°, isomeric with carbamic phenylhydrazide (p. 158), is obtained: 1. From its acetyl derivative, m.p. 169°, which is formed on boiling benzazide with acetohydrazide in acetone, nitrogen being evolved:



2. By the decomposition of acetone-phenylsemicarbazone,  $(\text{CH}_3)_2\text{C:NNH}\cdot\text{CO}\cdot\text{NHPh}$ , which is easily obtained by heating aniline with acetone-semicarbazone (*Borsche*, Ber. 38, 831). 3. From phenyl-urea by the action of hydrazine

hydrate. **Hydrazo-dicarboxylic anilide**,  $\text{PhNH}\cdot\text{CO}\cdot\text{NHNH}\cdot\text{CONHPh}$ , m.p.  $245^\circ$ , obtained by heating phenylsemicarbazide, is oxidised by nitric acid to **azo-dicarboxylic anilide**,  $\text{PhNHCO}\cdot\text{N}:\text{N}\cdot\text{CONHPh}$ , m.p.  $183^\circ$ . **Phenyl-carbamic azide**,  $\text{PhNH}\cdot\text{CON}_3$ , m.p.  $104^\circ$ , unlike other carboxylic azides, is decomposed by water or alcohol into  $\text{NH}_3$  and carbamic acid or its esters (*Curtius*, J. pr. [2], 58, 205).

**PHENYLATED DERIVATIVES OF THIOCARBAMIC ACIDS AND THIO-UREA.** **Phenyl-carbamic thiomethyl ester**,  $\text{PhNH}\cdot\text{COSCH}_3$ , m.p.  $83^\circ$ , and the **ethyl ester**, m.p.  $74^\circ$ , are obtained from diphenyl-amidine thioalkyls by the action of dilute sulphuric acid at  $180^\circ$ . (*Will*, Ber. 15, 339).

**Phenyl-thiourethane**, *xanthogen anilide*, *ethyl thiocarbanilate*,  $\text{PhNHCS}\cdot\text{OC}_2\text{H}_5$ , or  $\text{PhN}:\text{C}(\text{SH})\text{OC}_2\text{H}_5$ , m.p.  $71^\circ$ , is obtained from phenyl mustard oil by the action of alcohol at  $120^\circ$ , or by the action of alcoholic potash. It reacts with primary and secondary bases to form phenyl thioureas. On distillation it decomposes into phenyl mustard oil and alcohol (*Bamberger*, Ber. 15, 2164). Alkaline potassium ferricyanide oxidises it to ethoxy-phenyl mustard oil or ethoxy-benzthiazole (Vol. IV). Like the phenyl thioureas, it dissolves in alkalis and forms metallic compounds with silver, mercury, and lead.

**Phenyl-imido-thiocarboxylic acid**,  $\text{PhN}:\text{C}\begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$ , is not known, but its ethers are formed by the action of alkyl iodides on the phenyl-thiourethanes or their metallic compounds. The thioacetanilides (p. 89) and phenyl-thioureas (see below) react similarly. **Ethyl-methyl ester**,  $\text{PhN}:\text{C}\begin{smallmatrix} \text{OEt} \\ \text{SMe} \end{smallmatrix}$ , b.p.  $260^\circ$  (decomp.); **diethyl ester**, m.p.  $30^\circ$  (*Liebermann*, Ann. 207, 148).

**PHENYL-DITHIO-CARBAMIC ACID DERIVATIVES.** The free acid when liberated from its potassium salt, decomposes into aniline and  $\text{CS}_2$ . Its potassium salt,  $\text{PhNH}\cdot\text{CSSK}$ , is formed when potassium xanthogenate is boiled with aniline. It forms golden-yellow crystals (*Losanitsch*, Ber. 24, 3024). The ammonium salt,  $\text{PhNH}\cdot\text{CSSNH}_4$ , is obtained from aniline,  $\text{CS}_2$ , and aqueous ammonia (*Heller*, J. pr. 65, 369). For other aryl-thiocarbamates see *Losanitsch*, Ber. 40, 2970.

**Methyl-phenyl-dithiocarbamate**, m.p.  $87^\circ$ , and **phenyl-dithiourethane**, m.p.  $60^\circ$ , are formed from phenyl mustard oil and mercaptans on heating. They decompose into these substances again on heating to a higher temperature. They dis-

solve in alkalis. **Ethyl-phenyl-dithiourethane**,  $\text{C}_2\text{H}_5\text{N}(\text{C}_6\text{H}_5)_2\text{SSC}_2\text{H}_5$ , m.p.  $68^\circ$ , b.p.  $310^\circ$ , is obtained by heating diethyldiphenyl isothiurea with carbon disulphide to  $160^\circ$ . It is a very stable substance, insoluble in alkalis, and its sulphur is not removed by mercuric oxide or an alkaline lead solution. The phenyl-dithiourethanes, like phenyl-thiourethane and diphenyl-thiourea, give addition products when heated with methyl iodide (*Berntsen*, Ber. 15, 568; *Will*, Ber. 15, 1308).

**Sulphanhydride of phenylthiocarbamic acid**,  $\text{S}(\text{CSNHPh})_2$ , m.p.  $137^\circ$  (*Losanitsch*, Ber. 24, 3023).

**Methyl-phenyl-thiocarbamyl chloride**, m.p.  $35^\circ$ , is obtained from methyl-aniline and thiophosgene (*Billetter*, Ber. 20, 1631).

**PHENYL-THIOUREAS.** **Phenyl-thiourea**,  $\text{NH}_2\text{CSNHPh}$ , m.p.  $154^\circ$ , is obtained by the action of ammonia on phenyl mustard oil, or by the action of lead carbonate on ammonium phenyl-dithiocarbamate (*Heller*, J. pr. 65, 369). On heating with silver nitrate it is converted into phenyl-urea (p. 92), and with mercuric oxide it gives phenyl-cyanamide. With bromine in chloroform solution phenyl-thiourea reacts in the pseudo-form and gives the bromide of a disulphide  $\text{PhN}:\text{C}(\text{NH}_2)\text{SSC}(\text{NH}_2):\text{NPh}$ , m.p.  $128^\circ$  (*Hugershoff*, Ber. 34, 3130). With methyl iodide it gives the hydriodide of N-phenyl-methyl-isothiurea (p. 95). With acetic anhydride, the unstable *as*-phenyl-acetyl-thiourea,  $\text{PhN}(\text{COMe})\cdot\text{CSNH}_2$ , m.p.  $145^\circ$ , is first formed, and then isomerises on heating above the m.p. into the symmetrical form,  $\text{Ph}\cdot\text{NH}\cdot\text{CSNH}\cdot\text{COCH}_3$ , m.p.  $171^\circ$  (*Wheeler*, Am. Chem. J. 27, 257, 270; *Dixon and Taylor*, J. 93, 18). These reactions apply in general to aromatic thioureas.

**sym-Diphenyl-thiourea**, *thiocarbanilide*,  $\text{CS}(\text{NHPh})_2$ , m.p.  $151^\circ$ , forms colour-

less, glistening flakes, readily soluble in alcohol (*Losanitsch*, Ber. 19, 1821). It is obtained: 1. from phenyl isothiocyanate and aniline in alcoholic solution; 2. by boiling aniline with CS<sub>2</sub>, when H<sub>2</sub>S is eliminated; the formation of the compound is greatly facilitated by the addition of sulphur or H<sub>2</sub>O<sub>2</sub> (*Braun*, Ber. 39, 4369; but cf. *Snedker*, Chem. and Ind. 44, 74); 3. by heating phenyl mustard oil with thiourea (*Pieroni*, Gazz. 42, II, 183).

Reactions of thiocarbanilide are known in great number: 1. iodine converts it into phenyl isothiocyanate (p. 98) and  $\alpha$ -triphenyl-guanidine (p. 96); 2. it is decomposed into phenyl mustard oil and aniline by boiling conc. HCl. If mixed *sym*-thiocarbanilides, such as PhNH·CSNH·C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>H<sub>5</sub>, are subjected to this treatment they give two different mustard oils and two different bases (*Mainzer*, Ber. 16, 2016). 3. When treated with HgO carbanilide is formed. 4. In benzene solution with HgO it gives carbodiphenyl-imide (p. 99). 5. It gives diphenyl-guanidine with NH<sub>3</sub> and PbO; triphenyl-guanidine with aniline; oximido-diphenyl-urea, (PhNH)<sub>2</sub>C:NOH, with hydroxylamine; and amino-diphenyl-guanidine (p. 97) with hydrazine hydrate in the presence of alkali, etc. Phenyl- and *sym*-diphenyl-thioureas dissolved in alkalis; in the salts the metal is attached to sulphur (cf. thioacetanilide, p. 89).

For alkyl-phenyl-thioureas, see *Gebhardt*, Ber. 17, 2088; 23, 815; 26, 1636. *as*-Diphenyl-thiourea, m.p. 198°, is obtained from diphenylamine thiocyanate (*Werner*, Proc. 1892, 95). Triphenyl-thiourea, m.p. 152° (*Gebhardt*, Ber. 17, 2092). Tetraphenyl-thiourea, Ph<sub>2</sub>N·CS·NPh<sub>2</sub>, m.p. 195°, is obtained by heating triphenyl-guanidine with CS<sub>2</sub> (*Bernthsen*, Ber. 15, 1530).

**PHENYL-THIOHYDANTOINS.** While the product formerly believed to be thio-hydantoin has been shown to be isothiohydantoin, aromatic phenyl-thiohydantoins are known (*Marchwald*, Ber. 24, 3278): Phenyl- $\alpha$ -methyl-thiohydantoin, SC<NPh-CO or HSC<NPh-CO, m.p. 184°, is obtained by fusing phenyl mustard oil with alanine.

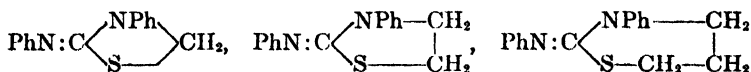
**PHENYLATED ISO-(PSEUDO-)THIOUREA DERIVATIVES.** Thiophenols (p. 213) will unite directly with cyanamide and its derivatives to produce thioureas with phenyl groups attached to sulphur: Ar·SH + CN·NH<sub>2</sub> = Ar·S·C(NH)(NH<sub>2</sub>). Phenyl-isothiourea, m.p. 96-97°, *p*-tolyl-isothiourea, m.p. 110° (decomp.); nitrate, m.p. 173°. The salt formed by 3 mols. of the base + 1 mol. HNO<sub>3</sub> + 1 mol. H<sub>2</sub>SO<sub>4</sub>, m.p. 253°, is very sparingly soluble in water and serves for the quantitative determination of HNO<sub>3</sub> (*Arnold*, Ann. 384, 322). N-Phenyl-thioureas and thiourea itself can be alkylated at the S atom by means of alkyl halides (*Bertram*, Ber. 25, 48).

N-Phenylmethyl-isothiourea,  $\text{PhNH} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} \begin{array}{c} \text{CSMe} \\ \text{NH} \end{array}$ , m.p. 71°, and *sym*-diphenyl-

methyl-isothiourea,  $\text{PhNH} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} \begin{array}{c} \text{CSMe} \\ \text{PhN} \end{array}$ , m.p. 110°, both give thiomethyl phenyl-

carbamate on heating with dilute sulphuric acid (p. 93) which proves that the methyl group is attached to sulphur. With alcoholic ammonia at 120° phenyl-guanidine (see below) and methyl mercaptan are formed. When heated with CS<sub>2</sub> the diphenyl compound gives phenyl mustard oil and methyl phenyl-dithiocarbamate (p. 94) (*Will*, Ber. 15, 343). The monophenyl compound reacts with acetyl chloride similarly to phenyl-thiourea (see above) with formation of an *as*-acetyl derivative, m.p. 86°, which changes to the symmetrical form when heated (*Wheeler*, Am. Chem. J. 27, 257, 270).

With CH<sub>2</sub>I<sub>2</sub>, CH<sub>2</sub>Br·CH<sub>2</sub>Br, CH<sub>2</sub>Br·CH<sub>2</sub>·CH<sub>2</sub>Br, diphenyl-thiourea gives cyclic derivatives of isothiourea (*Foerster*, Ber. 21, 1872):



The second and third compounds are derivatives of thiazole and thiazine, respectively.



**Tetraphenyl-isothioureia**,  $\begin{matrix} \text{Ph}_2\text{N} \\ \text{PhN} \end{matrix} \begin{matrix} \diagup \\ \diagdown \end{matrix} \text{CSPh}$ , m.p. 185–188°, has been obtained by the reaction between triphenyl-chlorocarbamidine (p. 96) and sodio-thiophenol (*Steindorff*, Ber. 37, 965).

**Phenyl-isothio-hydantoic acid**,  $\text{HN}:\text{C} \begin{matrix} \diagup \text{NHPH} \\ \diagdown \text{SCH}_2\text{CO}_2\text{H} \end{matrix}$ , m.p. 150° (*Rizzo*, Gazz.

28, I, 356) and **diphenyl-isothio-hydantoic acid**,  $\text{PhN}:\text{C} \begin{matrix} \diagup \text{NHPH} \\ \diagdown \text{SCH}_2\text{CO}_2\text{H} \end{matrix}$ , are obtained from phenyl- and diphenyl-thioureas by the action of chloroacetic acid. By dehydration these compounds give isothiohydantoin: an unstable **phenyl-isothiohydantoin**,  $\text{HN}:\text{C} \begin{matrix} \diagup \text{NPh-CO} \\ \diagdown \text{S-CH}_2 \end{matrix}$ , m.p. 148°, which changes above 100° to the

stable isomer,  $\text{PhN}:\text{C} \begin{matrix} \diagup \text{NH-CO} \\ \diagdown \text{S-CH}_2 \end{matrix}$ , m.p. 178°. The former is also obtained from

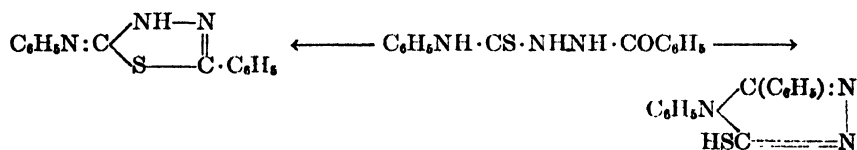
**thiocyano-acetanilide**,  $\text{CNS} \cdot \text{CH}_2\text{CONHPh}$ , m.p. 91°, on heating to 100°; the latter, on boiling with HCl is first converted into phenyl-isothiohydantoic acid by ring opening, and subsequently gives a mixture of mustard oil acetic acid

(Vol. I, p. 526) and **phenyl mustard oil acetic acid**,  $\text{CO} \begin{matrix} \diagup \text{NPh-CO} \\ \diagdown \text{S-CH}_2 \end{matrix}$  (*Wheeler*,

Am. Chem. J. 28, 121), which latter is also obtained by the hydrolysis of **diphenyl-isothiohydantoin**,  $\text{PhN}:\text{C} \begin{matrix} \diagup \text{NPh-CO} \\ \diagdown \text{S-CH}_2 \end{matrix}$ , m.p. 176°.

**HYDROXYLAMINE AND HYDRAZINE DERIVATIVES OF PHENYLATED THIOUREAS.** **Phenyl-hydroxyl-thiourea**,  $\text{PhNHCSNHOH}$ , m.p. 106°, from hydroxylamine and phenyl mustard oil, decomposes readily into water, sulphur, and phenyl-cyanamide (*Voltmer*, Ber. 24, 378).

**Phenyl-thiosemicarbazide**, **phenyl-thiocarbamic hydrazide**,  $\text{PhNH} \cdot \text{CS} \cdot \text{NH} \cdot \text{NH}_2$ , m.p. 140° (decomp.), is obtained from phenyl mustard oil and hydrazine hydrate, or from diphenyl-thiourea with hydrazine hydrate in alcoholic solution (*Busch*, Ber. 33, 1058). It reacts with aldehydes to form phenyl-thiosemicarbazones. Its acetyl derivatives readily lose water and form thiobiazolines (Vol. IV); its benzoyl derivative gives a phenyl-imido-phenylthiobiazoline on dehydration with acetyl chloride, but a diphenyl-triazole mercaptan (see triazoles, Vol. IV) with benzoyl chloride (*Marckwald*, Ber. 29, 2914):



**PHENYLATED GUANIDINE DERIVATIVES:** **Phenyl-guanidine**, m.p. 60°,

$\text{NH}:\text{C} \begin{matrix} \diagup \text{NHPH} \\ \diagdown \text{NH}_2 \end{matrix}$ , is obtained from cyanamide and aniline hydrochloride. *sym*-

**Diphenyl-guanidine**, *melaniline*,  $\text{NH}:\text{C}(\text{NHPH})_2$ , m.p. 147°, is obtained similarly from cyano-anilide (p. 99) and aniline hydrochloride, and therefore also by the action of cyanogen chloride on dry aniline (U. S. Pat. 1,727,060). Like guanidine itself, these two compounds are monacid bases. Diphenyl-guanidine is used as an accelerator in the vulcanisation of rubber. It is decomposed by  $\text{CS}_2$  into diphenyl-thiourea and thiocyanic acid. *as*-**Diphenyl-guanidine**,  $\text{Ph}_2\text{NC}(\text{NH})\text{NH}_2$ , m.p. 147°, is obtained from diphenylamine and cyanamide.

**$\alpha$ -Triphenyl-guanidine**,  $\text{PhN}:(\text{NHPH})_2$ , m.p. 143°, is obtained by heating diphenyl-urea or diphenyl-thiourea at 140°, alone, or with copper, or by warming an alcoholic solution of diphenyl-thiourea and aniline with  $\text{Pb}(\text{OH})_2$  (*Wheeler*,

Am. Chem. J. 28, 121), or  $\text{HgO}$ , or boiling it with iodine solution. It is decomposed by  $\text{CS}_2$  into diphenyl-thiourea and phenyl-isothio-cyanate (p. 98).

**$\beta$ -Triphenyl-guanidine**,  $\text{HN}:\text{C} \begin{smallmatrix} \text{NPh}_2 \\ \text{NHPH} \end{smallmatrix}$ , m.p.  $131^\circ$ , has been obtained by heating cyananilide with diphenylamine hydrochloride. It is decomposed by  $\text{CS}_2$  into diphenylamine, phenyl mustard oil, and thiocyanic acid. ***sym*-Tetraphenyl-guanidine**,  $\text{NH}:\text{C}[\text{N}(\text{C}_6\text{H}_5)_2]_2$ , m.p.  $130^\circ$ , is obtained by the action of cyanogen chloride on diphenylamine at  $170^\circ$ .

***as*-Tetraphenyl-guanidine**,  $\text{PhN}:\text{C} \begin{smallmatrix} \text{NPh}_2 \\ \text{NHPH} \end{smallmatrix}$ , m.p.  $140^\circ$ , and **pentaphenyl-guanidine**,  $\text{PhN}:\text{C}[\text{N}(\text{C}_6\text{H}_5)_2]_2$ , m.p.  $179^\circ$ , are obtained from aniline and diphenylamine, respectively, with triphenyl-chlorocarbamidine (p. 93).

**Amino-diphenyl-guanidine**,  $\text{PhN}:\text{C}[\text{NHPH}]\text{NH}\cdot\text{NH}_2$ , m.p.  $99^\circ$ , is obtained from diphenyl-thiourea by the action of hydrazine hydrate in alcoholic-alkaline solution (without alkali phenyl-thiosemicarbazide is formed). It is a strong base, forms addition compounds with aniline, and with carboxylic acids and nitrous acid it condenses to triazole and tetrazole derivatives (*Busch*, Ber. 33, 1058; 35, 1710).

**Diphenyl-hydroxyguanidine**,  $\text{HON}:\text{C}(\text{NHPH})_2$ , m.p.  $151^\circ$ , is obtained from diphenyl-thiourea by the action of alcoholic hydroxylamine and  $\text{PbO}$  (*Stollé*, Ber. 32, 2238).

#### PHENYL-BIGUANIDES.

**$\alpha$ -Phenyl-biguanide**,  $\text{NH} \begin{smallmatrix} \text{NH} \\ \text{NH}_2 \end{smallmatrix} \text{C} \cdot \text{NH} \cdot \text{C} \begin{smallmatrix} \text{NH} \\ \text{NHPH} \end{smallmatrix}$ , hydrochloride; m.p.  $237^\circ$ , is obtained by heating aniline hydrochloride with dicyano-diamide (*Lumière*, Bull. 33, 205; *Hermann*, Mo. 26, 1021).  **$\alpha$ -Diphenyl-biguanide**,  $\text{NH} \begin{smallmatrix} \text{NH} \\ \text{NH}_2 \end{smallmatrix} \text{C} \cdot \text{NH} \cdot \text{C} \begin{smallmatrix} \text{NPh} \\ \text{NHPH} \end{smallmatrix}$ , m.p.  $167^\circ$  is obtained from thiocarbamilide and guanidine (*Beutel*, Ann. 310, 335; *Cramer*, Ber. 34, 2594).

**PHENYLATED NITRILES AND IMIDES OF CARBONIC ACID.** **Phenyl isocyanate**, *carbanil*,  $\text{C}_6\text{H}_5\text{N}:\text{C}=\text{O}$ , b.p.  $166^\circ$ , a liquid with an acid smell, is obtained: 1. by distilling oxanilide, or 2. a phenylurethane with  $\text{P}_2\text{O}_5$  (*Goldschmidt*, Ber. 25, 2578, footnote); 3. from diazonium salts by the action of potassium cyanate and copper (*Gallermann*, Ber. 35, 1086); 4. from phenyl mustard oil  $\text{PhN}:\text{CS}$ , by the action of  $\text{HgO}$  (*Kuhn*, Ber. 23, 1536). at  $170^\circ$ ; 5. by the action of thionyl chloride on benzohydroxamic acid (*q.v.*) in benzene (*Marquis*, C.R. 143, 1163); 6. by warming benzoyl azide (*q.v.*) or benzoyl chloride and sodium azide in an indifferent solvent (*Stoerner*, Ber. 42, 3133; *Schroeter*, *ibid.*, 3359); 7. by the action of nitrous acid on monophenyl-urea in the presence of an excess of  $\text{HCl}$  (*Haager*, Mo. 26, 267); 8. by the action of phosgene on aniline or, better, its hydrochloride; 9. a small quantity of phenyl isocyanate was detected in an aqueous solution of potassium chlorobenzamide which had been heated with potassium dibenzo-hydroxamate (*Mohr*, J. pr. 72, 306). By methods 6, 7, and 8, a number of substituted carbanils have been prepared (*Villnet*, Bull. [3] 21, 952; Ger. Pat. 133,760).

The reactions of phenyl isocyanate resemble those of the alkyl isocyanates. Water converts it into diphenyl-urea (p. 92), and alkalis into phenyl-carbamates (*Mohr*, J. pr. 73, 177). It combines with alcohols and phenols to form phenyl-urethanes, a reaction which is used to prove the presence of an alcoholic hydroxyl group in a compound, and for purposes of identification (*Snape*, Ber. 18, 2428; *Tesmer*, *ibid.*, 2606). Similar reactions take place with the  $\text{SH}$ -group, and the  $\text{OH}$ -group of aldoximes and ketoximes, but not with  $\text{C}=\text{O}$  and  $\text{C}=\text{S}$  groups. (*Goldschmidt*, Ber. 25, 2578). On the other hand, it combines with 1,3-dicarbonyl compounds, such as acetyl-acetone, acetoacetic ester, malonic ester, *etc.*, in the presence of small quantities of alkali, forming *O*-carbanilido-derivatives, *e.g.*,  $\text{PhNHCOC}(\text{COCH}_3)_2\text{CO}_2\text{R}$ . These, unlike the *O*-carbanilido-derivatives, are acidic, and give the ferric chloride reaction (*Dieckmann*, Ber. 37, 4627).

Phenyl isocyanate gives phenyl-urea (p. 92) with ammonia; with bromine it gives the dibromide,  $\text{PhNCOBr}_2$ , m.p.  $144^\circ$ , also obtained by the action of bromine on benzoyl azide (J. pr. 87, 513). With diazo-amino compounds,  $\text{PhN}_2\cdot$

NHR', mixed ureas are produced, in which the hydrogen of the NH-group is replaced by the residue  $-\text{CONH}\cdot\text{Ph}$  (p. 128; *Goldschmidt*, Ber. 22, 3109). For the action with hydroxy-acids, see *Lambling*, Bull. 29, 122; with phenyl magnesium bromide, urethanes, and ureas, *Lakra*, Am. 51, 2220; *Gilman*, *ibid.*, 2252.

All these reactions of phenyl isocyanates, if taking place in the absence of a solvent, go on normally without rearrangements, and are therefore valuable for the determination of constitution (*Goldschmidt*, Ber. 23, 2179; *Dieckmann*, Ber. 33, 2002; 37, 4632; *Michael*, Ber. 38, 22).

By heating phenyl isocyanate with benzene and aluminium chloride, benzanilide is obtained; see syntheses of benzoic and homologous acids.

*p*-Nitrophenyl-isocyanate, m.p. 56°, is obtained by the action of carbonyl chloride on *p*-nitraniline (*Cox*, Org. Synth. 14, 72).

Dicarbanil,  $\text{PhN} \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{NPh}$ , m.p. 175°, obtained by the action of triethyl-

phosphine or pyridine on phenyl isocyanate (*Snape*, J. 49, 254). Tricarbanil, m.p. 274°.

*o*-, *m*-, *p*-Tolyl isocyanates,  $\text{CH}_3\text{C}_6\text{H}_4\text{N}:\text{CO}$ , b.p. 186°, 196°, and 187°, respectively, are obtained by method 7.

Triphenyl isocyanurate,  $\text{C}_3\text{O}_3(\text{NPh})_3$ , m.p. 275°, is obtained (1) by the polymerisation of phenyl isocyanate on heating with potassium acetate (*Hofmann*, Ber. 18, 3225); (2) by the action of conc. HCl on triphenyl-isomelamine (p. 100) at 150°.

Triphenyl cyanurate,  $\text{C}_3\text{N}_3(\text{OPh})_3$ , m.p. 224°, is obtained by the action of cyanogen chloride or cyanuric chloride on sodium phenate.

Isocyano-phenyl chloride, *phenylimido-carbonyl chloride*,  $\text{PhN}:\text{CCl}_2$ , b.p. 210° (corr.) is a colourless oil with a pungent smell, which has an irritating effect on the eyes and lungs. It is prepared from phenyl isocyanide (p. 90) by the action of chlorine in chloroform, or from phenyl mustard oil by the action of chlorine (*Freund*, Ber. 26, 2870). With aniline it forms  $\alpha$ -triphenyl-guanidine (*Nef*, Ann. 270, 282).

Phenyl thiocyanate,  $\text{PhSCN}$ , b.p. 245°, is isomeric with phenyl-mustard oil, and with benzthiazole,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{S} \\ \diagdown \text{N} \end{array} \text{CH}$  (see amino-thiophenols, p. 213). It is ob-

tained from (1) the action of HSCN on benzene-diazonium sulphate (p. 125); (2) the action of cyanogen chloride on lead thiophenate. It behaves like the alkyl thiocyanates. For condensation with resorcinol, see *Borsche*, Ber. 62, 1743. For nitration of phenyl thiocyanate and other aromatic thiocyanates see *Challenger*, J. 1930, 26.

**PHENYL ISOTHIOCYANATE**, *phenyl-mustard oil*,  $\text{C}_6\text{H}_5\text{N}:\text{CS}$ , m.p.  $-21^\circ$ , b.p. 222°, is a colourless liquid smelling of mustard oil. It is prepared: 1. from diphenyl-thiourea (p. 95) by loss of aniline by the action of hot sulphuric acid, conc. HCl, acetyl chloride (*Hunter*, Chem. News 130, 401), or, best, conc. phosphoric acid (*A. W. Hofmann*, Ber. 15, 986); 2. together with triphenyl-guanidine (p. 97) from diphenyl-thiourea by the action of alcoholic iodine solution; 3. by the action of thiophosgene on aniline; 4. by the action of nitrous acid on phenyl thiourea (*Haager*, Mo. 27, 267); 5. from salts of phenyl dithiocarbamic acid (p. 94) by the action of phosgene (*Slota*, Ber. 63, 888) or, preferably, by distilling the ammonium salt with lead nitrate, a general method of preparing the aryl mustard oils (*Davis*, Org. Synth. 1, 437).

When heated with copper or zinc dust it is converted into benzonitrile, owing to a rearrangement of the phenyl isocyanide first formed (p. 90). When heated with anhydrous alcohols to 120°, or with alcoholic potash, it is converted into phenyl thiourethanes (p. 94) (*Orndorff*, Am. Chem. J. 22, 458). With ammonia, aniline, hydrazine, hydroxylamine it gives phenyl-thioureas (p. 94), and with chlorine isocyanophenyl chloride is formed. It combines with sodio-malonate ester to give thiocarbanilino-malonate ester,  $\text{PhNHCS}\cdot\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2$  (*Ruheman*, J. 93, 621); with KCN it gives the potassium salt of thio-oxanilic nitrile,  $\text{PhNH}\cdot\text{CS}\cdot\text{CN}$ , m.p. 82° (*Reisert*, Ber. 57, 981); with aromatic hydrocarbons, phenols, phenyl ethers, and thiophenol ethers, in the presence of aluminium chloride it gives carboxylic thioanilides (*Gattermann*, J. pr. 59, 572); with sodio-

acetoacetic ester it gives an addition product, which, on acidifying, yields the monothioanilide of acetyl-malonic ester,  $\text{CH}_3\text{CO}\cdot\text{CH}(\text{CS}\cdot\text{NHPh})\text{COOC}_2\text{H}_5$ , m.p. 82–83° (*Brewster*, *Am.* 40, 406); with alkyl-magnesium iodide it gives salts which are decomposed by acids to thio-anilides of fatty acids, e.g.,  $\text{PhNCS}$

$\xrightarrow{\text{Me Mg I}}$   $\text{PhNH}\cdot\text{CS}\cdot\text{Me}$  (*Sachs*, *Ber.* 36, 585). By reduction with Zn and HCl, phenyl mustard oil gives aniline and thioformaldehyde, but with aluminum amalgam it gives thiocarbaniide and methyl mercaptan (*Gulbier*, *Ber.* 34, 2033). Phenyl mustard oil may be used for identifying primary amines (*Ottobacher*, *Am.* 51, 1909).

*o*-, *m*-, and *p*-Tolyl isothiocyanates, b.p. 239°, 244°, and 236°, respectively; m.p. of the *p*-compound, 26°; **mesityl isothiocyanate**, m.p. 63°, which has a pleasant odour, is obtained by method 3 (*Dyson*, *Chem.* and *Ind.* 48, 81). The odour and constitution of chlorinated homologous mustard oils are discussed by *Dyson*, *Perfumery* 1928, 19, 171.

**POLYSULPHIDES OF ARYL MUSTARD OILS**,  $\text{Ar}\cdot\text{N}:\text{C}=\text{S}$  are obtained

from aryl ammonium dithiocarbamates by the action of  $\text{S}_2\text{Cl}_2$ ; **Phenyl mustard oil hexasulphide** ( $n = 6$ ) is a canary-yellow powder (*Levi*, *Gazz.* 61, 619).

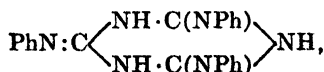
**Selenophenyl mustard oil**,  $\text{C}_6\text{H}_5\text{N}:\text{CSe}$ , b.p. (6–8 mm.) 120–130° (decompn.), is obtained from isocyanophenyl-chloride (p. 90) by the action of sodium selenide (*Hasan*, *Hunter*, *J.* 1935, 1762).

**PHENYLATED CYANAMIDE DERIVATIVES**. (Cf. cyanamide, Vol. I, p. 528.) **Phenyl-cyanamide**, *cyananilide*,  $\text{PhNHCN} + \frac{1}{2}\text{H}_2\text{O}$ , m.p. 47°, loses its water of crystallisation in a desiccator, and liquefies; in moist air the hydrate is reformed. On prolonged standing, or on heating, it polymerises to triphenyl-isomelamine. It is obtained: 1. by passing cyanogen chloride into an ethereal solution of aniline; 2. by heating phenyl-thiourea (p. 94) with HgO or lead acetate and alkali (*Hofmann*, *Ber.* 18, 3220). It dissolves readily in alcohol and ether. With  $\text{H}_2\text{S}$  it regenerates phenyl-thiourea. For substituted phenyl-cyanamides see *Pierron*, *Bull.* 33, 69: 35, 1197.

**Phenyl-methyl-cyanamide**,  $\text{PhMeN}\cdot\text{CN}$ , m.p. 30°, is obtained from phenyl-cyanamide and  $\text{CH}_3\text{I}$  by the action of sodium ethoxide (*Traube*, *Ber.* 33, 1383); or from mono- or dimethyl-aniline by the action of cyanogen bromide. The last reaction, the action of cyanogen bromide on dialkyl-anilines, has yielded a number of homologous phenyl-alkyl-cyanamides (*Braun*, *Ber.* 33, 2728; 35, 1279). **Diphenyl-cyanamide**,  $\text{Ph}_2\text{N}\cdot\text{CN}$ , m.p. 73°, is obtained from *as*-diphenyl-thiourea (p. 95) by the action of ammoniacal silver solution (*Werner*, *Ber.* 26 R 607).

**Carbo-diphenylimide**,  $\text{PhN}:\text{C}:\text{NPh}$ , is a viscous liquid, b.p. (30 mm.) 218°. On distillation at ordinary pressure, carbo-diphenylimide partly rearranges to a trimeric form, m.p. 161° (*Miller*, *Ber.* 28, 1004; *Schall*, *Ber.* 29, 270). It is obtained 1. by the action of HgO on a solution of *sym*-diphenyl-thiourea (p. 95) in benzene; 2. by distilling  $\alpha$ -triphenyl-guanidine (p. 96); and 3. from phenyl isocyanate at 180°, when  $\text{CO}_2$  is lost (*Stolle*, *Ber.* 41, 1125). It combines with water to give *sym*-diphenyl-urea, with  $\text{H}_2\text{S}$  to give *sym*-diphenyl-thiourea, with aniline to give  $\alpha$ -triphenyl-guanidine (cf. *o*-phenylene-diamine, p. 106), and with phenol to give diphenyl-isourea phenyl ether (*Busch*, *J.* pr. 79, 513). When HCl is passed through a benzene solution of carbo-diphenylimide the compounds  $\text{PhN}:\text{CCl}\cdot\text{NPh}$ , and  $\text{PhNH}\cdot\text{CCl}_2\cdot\text{NPh}$  are formed (*Leugfeld*, *Am. Chem. J.* 17, 98). With malonic ester and similar compounds carbo-diphenylimide combines to give substances of the type  $\text{PhNH}\cdot\text{CNPh}\cdot\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2$  (*Traube*, *Ber.* 32, 3176). Aliphatic and thio-aliphatic acids also combine with it, and compounds such as *acetyl-diphenyl urea*, and *acetyl-diphenyl-thiourea* are formed (*Schall*, *J.* pr. 64, 261). With alkyl-magnesium iodides, compounds containing Mg are obtained, which give diphenyl-amidines (p. 89) when acted upon by acids **Carbo-di-*p*-tolylimide**,  $(\text{C}_7\text{H}_7\text{N})_2\text{C}$ , m.p. 57–59°.

**Triphenyl-melamine**, *triphenyl-cyanuric-triamide*,



m.p. 228°, is obtained by the action of cyanuric chloride on aniline, or from methyl trithio-cyanurate and aniline at 250–300°.

**Hexaphenyl-melamine**,  $C_6N_3(NPh)_3$ , m.p. 300°, is obtained from cyanuric chloride and diphenylamine.

**Triphenyl-isomelamine**,  $NH:C \begin{matrix} \swarrow NPh \cdot C(NH) \\ \searrow NPh \cdot C(NH) \end{matrix} NPh$ , m.p. 210°, is formed as

a polymerisation product of phenyl-cyanamide (p. 99), in the form of an addition product of two mols. of the base with one mol. of phenyl-cyanamide (m.p. 185°). On heating with HCl the NH-groups are successively replaced by O, and finally isocyanuric triphenyl ester is formed (p. 98). In addition to normal and triphenyl-isomelamine, asymmetrical triphenyl-melamines are known (*Hofmann*, Ber. 18, 3218, 3225, 3228).

**ANILIDES OF DICARBOXYLIC ACIDS.** Oxalic acid and its homologues as well as the unsaturated dicarboxylic acids form anilic acids and di-anilides. Those dicarboxylic acids which are capable of forming anhydrides give also N-phenylimides. Anilic acids are obtained: 1. by partial hydrolysis of dianilides, 2. by mixing ether or chloroform solutions of an anhydride and of aniline (*Anschtz*, Ber. 20, 3214), 3. by hydrolysis of N-phenylimides (*Anschtz*, Ber. 31, 957). The N-phenylimides are reformed from the anilic acids by treatment with PCl<sub>5</sub> or acetyl chloride, and are also formed when the acids or anhydrides are heated with aniline. A large number of these compounds have been mentioned in Vol. I in connection with their respective acids.

**PHENYLAMINO DERIVATIVES OF OXALIC ACID.** **Oxanilic acid**,  $PhNH \cdot CO \cdot CO_2H$ , m.p. 150° (for an isomeric oxanilic acid, m.p. 210°, see *Nef*, Ann. 270, 295) is obtained by heating oxalic acid with aniline, from oxanilide by the action of alcoholic potash, and from citracon-anilic acid by oxidation with permanganate. **Methyl ester**, m.p. 114° (*Anschtz*, Ann. 254, 10). **Ethyl ester**, m.p. 66°. **Chloride**, m.p. 82° (*Aschan*, Ber. 23, 1820).

**Oxanilic nitrile**, *cyano-formanilide*,  $PhNHCOCN$ , m.p. 120°, is obtained by adding HCN to phenyl isocyanate. Heated above its melting point it decomposes into its components. By careful hydrolysis it yields **phenyl-oxamide**,  $PhNHCO \cdot CONH_2$ , m.p. 224°, and on addition of H<sub>2</sub>S it gives **oxanilic thioamide**,  $PhNH \cdot COCSNH_2$ , m.p. 176° (*Duckmann*, Ber. 38, 2978).

**OXANILIDE**,  $(CONHPh)_2$ , m.p. 245°, is obtained from the isomeric di-N-phenyl ether of glyoxime,  $Ph \cdot NO=CH-CH=NO \cdot Ph$ , m.p. 183° (decomp.), by rearrangement under the influence of AcOH and acetic anhydride. The glyoxime derivative is obtained: 1. from nitrosobenzene and diazomethane, and 2. from N-phenylhydroxylamine and glyoxal on formaldehyde (p. 69) (*Pechmann*, Ber. 39, 2871; *Bamberger*, Ber. 35, 1883).

A number of sulphur derivatives of oxanilic acid are obtained by the action of P<sub>2</sub>S<sub>5</sub> on the corresponding oxygen compounds; they are distinguished by their intense yellow to orange colours (*Reissert*, Ber. 37, 3708). **Thio-oxanilic acid**,  $PhNHCSCO_2H$ , m.p. 102°. **Thio-oxanilide**,  $PhNHCS \cdot CONHPh$ , m.p. 145°. Both these compounds are readily converted into derivatives of benzthiazole (Vol. IV). **Thio-oxanilic thioamide**,  $PhNHCS \cdot CSNH_2$ , m.p. 98°. **Dithio-oxanilide**,  $(CSNHPh)_2$ , m.p. 134°, can also be obtained by the action of H<sub>2</sub>S on oxanilide chloride (*Sabanajev*, C. 1902, II, 121).

**Tetra-p-tolyl-oxamide**,  $[CON(C_6H_4 \cdot Me)_2]_2$ , m.p. 127°, is obtained from p-ditolyl-urea chloride (p. 92). **Oxanilido-dioxime**,  $[C:(NOH)NHP]_2$ , m.p. 215° (decomp.) is obtained from *dibromoglyoxime peroxide*. **Semiortho-oxalic dianilido methyl ester**,  $MeO_2C \cdot C(NHPh)_2OMe$ , and **phenylimido-oxalic dimethyl ester**,  $MeO_2C \cdot C:NHPh(OMe)$ , m.p. 111°, are obtained from dichlor-oxalic ester and aniline (*Anschtz*, Ber. 28, 60). **Oxanilic diphenyl-amidine**,

$PhNHCO \cdot C \begin{matrix} \swarrow NHP \\ \searrow NPh \end{matrix}$ , m.p. 134°, is obtained from semiortho-oxalic ester and

from *ethyl dichloro-oxanilate* (*Klinger*, Ann. 184, 268). The corresponding nitrile, *carbo-diphenyl-imido-hydrocyanide*,  $NC \cdot C(NHPh):NPh$ , is obtained by the action of HCN on carbo-diphenylimide (see p. 99); with yellow ammonium sulphide it gives a thio-amide,  $NH_2CS \cdot C(NHPh):NPh$ , which is readily converted into *isatin anilide* and *indigo* (Vol. IV). *o*-Nitro-oxanilic acid, m.p. 112°, and *o*-dinitro-oxanilide, see *Hübner*, Ann. 209, 369.

**Malonanilic acid**,  $\text{PhNHCOCH}_2\text{CO}_2\text{H}$ , melts at  $132^\circ$  with decomp. into  $\text{CO}_2$  and acetanilide. It is also obtained by a rearrangement of sodium acetyl-phenyl-carbamate at  $140^\circ$ . The latter compound is prepared from sodio-acetanilide and  $\text{CO}_2$  (Seifert, Ber. 18, 1359). **Malonanilide**,  $\text{CH}_2(\text{CONHPh})_2$ , m.p.  $223^\circ$  (Freund, Ber. 17, 134); **malonic methyl anilide** (Vorländer, Ber. 31, 1826); **dithiomalonanilide**,  $\text{CH}_2(\text{CSNHPh})_2$ , m.p.  $149^\circ$ , is obtained from malonanilide by the action of  $\text{P}_2\text{S}_5$  (Reissert, Ber. 39, 3300).

**Succinanilic acid**, **succinanil**, see Vol. I, p. 552; **succinimide**.

**Fumaranilic acid**, **fumaranilic chloride**, **fumaric dianilide**, **maleinanilic acid**, **maleinanil**, **dichloromaleinanil**, **dichloromaleinanil dichloride**, **dichloromaleinanil-dimethyl ester**, **dichloromaleinimidanil**, **dichloromaleindianil**, **citraconanilic acid**, **citracon-anil**, **itacon-anilic acid**, see Vol. I in connection with the corresponding carboxylic acids.

**ANILIDO-DICARBOXYLIC ACIDS**. **Anilido-malonic acid**,  $\text{PhNH}\cdot\text{CH}(\text{COOH})_2$ , melts at  $119^\circ$  with loss of  $\text{CO}_2$ , and formation of phenylglycine (p. 90). Its esters, (methyl, m.p.  $68^\circ$ , ethyl, m.p.  $45^\circ$ ) are obtained from the bromo-malonic esters by the action of aniline, and behave like malonic esters; they can be alkylated on the C-atom, they add on  $\alpha,\beta$ -unsaturated carboxylic esters, etc. (see Vol. I, 543). At  $260$ – $265^\circ$  they condense to *indoxyl esters*, and these are readily converted into indigo (Conrad, Ber. 35, 511). For the action of nitrous acid see Curtiss, Am. Chem. J. 28, 315).

**Phenyl-asparaginilic acid**, **phenyl-asparaginil**;  $\alpha$ -**anilido-pyrotartaric acid**; **pseudo-itaconanilic acid**; see amino-succinic acids, Vol. I, p. 608.

**PHENYLATED UREIDES OF DICARBOXYLIC ACIDS**. **Phenyl-parabanic**

**acid**,  $\text{CO} \begin{array}{c} \text{NPh}-\text{CO} \\ | \\ \text{NH}-\text{CO} \end{array}$ , m.p.  $208^\circ$ , and **diphenyl-parabanic acid**, m.p.  $204^\circ$ , are

obtained from the corresponding carbamides by the action of ethoxalic chloride (Stojentin, J. pr. 32, 20). **Diphenyl-malonyl-urea**, **diphenyl-barbituric acid**,

$\text{CO} \begin{array}{c} \text{NPh}-\text{CO} \\ | \\ \text{NPh}-\text{CO} \end{array} \text{CH}_2$ , m.p.  $233^\circ$ , is obtained by the action of malonyl chloride

on carbanilide. By a sequence of reactions similar to those leading from malonyl-urea to uric acid (Vol. I, p. 639) diphenyl-malonyl-urea gives **diphenyl-violuric acid**, m.p.  $227^\circ$ , **diphenyl-uramil**, m.p.  $195^\circ$ , **diphenyl- $\psi$ -uric acid**, m.p.  $217^\circ$ , and **1,3-diphenyl-uric acid**, m.p.  $300^\circ$  (Cohen, Proc. 1907, 148).

**SUBSTITUTION PRODUCTS OF ANILINE**. Special interest attaches to the substitution products of aniline, because the substitution rules for aromatic amines have been derived from them, and because they are the connecting links in many determinations of constitution. The substitution products of other primary phenylamines are of lesser interest.

**HALOGEN DERIVATIVES OF ANILINE**. *Methods of formation*.—1. Aniline, like phenol, is much more readily substituted than benzene. If chlorine or bromine water is allowed to act on aqueous solutions of aniline salts, halogen atoms enter the 2, 4, and 6 positions. For intermediate addition products see Hantzsch, Ber. 38, 2159; Fries, Ann. 376, 128.

Starting with acetanilide (p. 88) the first products obtained by the action of  $\text{Cl}_2$  or  $\text{Br}_2$  are the *p*- and *o*-mono-substitution products, which may be converted into *o,p*-di-substitution products. When, on the other hand,  $\text{Cl}_2$  or  $\text{Br}_2$  acts on aniline in presence of conc. sulphuric acid, *m*-compounds are formed, as the positively charged  $-\text{NH}_3^+$  group of aniline sulphate is a *m*-directing group (see p. 15). For the further substitution of *m*-substituted anilines see Langer, Ber. 15, 1328. Iodine directly substitutes in the aniline nucleus, the HI formed combining with the excess of aniline:



(cf. non-iodination of benzene, etc.).

2. Monohalogen-anilines are smoothly obtained from monohalogen-nitro-compounds, prepared from nitramino-compounds *via* the diazo-compounds.

5. *p*-Chloro-anilines are obtained by heating *p*-chloro-bromobenzenes with aqueous  $\text{NH}_3$ , in the presence of  $\text{Cu}_2\text{O}$  at  $120^\circ$  in a sealed tube. *p*-Chloro-aniline is formed when nitrobenzene is reduced in a strong hydrochloric acid solution (p. 88 and *Stieglitz*, *Am. Chem. J.* **31**, 453; *Blanksma*, *Rec.* **25**, 365).

*p*-Chloro-aniline is a stronger base than the *o*- and *m*-compounds (Ber. **10**, 974). The dipole moments are: *m*-chloro-aniline, 2.6–2.7 D., *p*-chloro-aniline, 2.9 D.

| Compound                            | 1,2- <i>o</i> - |                  | 1,3- <i>m</i> - |                     | 1,4- <i>p</i> - |                  |
|-------------------------------------|-----------------|------------------|-----------------|---------------------|-----------------|------------------|
|                                     | M.p.            | B.p.             | M.p.            | B.p.                | M.p.            | B.p.             |
| $\text{FC}_6\text{H}_4\text{NH}_2$  | –28.95          | 94.6<br>(55 mm.) | Liquid          | 186.1<br>(753–756)  | –0.82           | 197<br>(753 mm.) |
| $\text{ClC}_6\text{H}_4\text{NH}_2$ | –2.1            | 207.0            | –10.2           | 228.5               | 69.69           | 232.3            |
| $\text{BrC}_6\text{H}_4\text{NH}_2$ | 29.4            | 229              | 16.7            | 251                 | 66.4            | Dec.             |
| $\text{IC}_6\text{H}_4\text{NH}_2$  | 56.5            | ..               | 27              | 145–146<br>(15 mm.) | 62–63           | ..               |

Of the higher halogen substitution products of aniline the following may be mentioned:

From acetanilide:

2,4-Dichloroaniline, m.p.  $63^\circ$ , b.p.  $245^\circ$  (*Witt*, Ber. **7**, 1602).

2,4-Dibromoaniline, m.p.  $79^\circ$ .

From the corresponding nitro-compounds:

2,5-Difluoroaniline, b.p. (30 mm.)  $84.5\text{--}85.8^\circ$  (*Swarts*, Belg. **1914**, 176).

2,5-Dichloroaniline, m.p.  $50^\circ$ , b.p.  $246^\circ$  (*Noelting*, Ber. **38**, 3506).

2,5-Dibromoaniline, m.p.  $51^\circ$  (*Meyer*, Ann. **165**, 180).

2,6-Diiodoaniline, m.p.  $122^\circ$  (*Brenans*, C.r. **138**, 153).

2,4-Diiodoaniline, m.p.  $96^\circ$  (*Brenans*, C.r. **139**, 63).

From aniline by the action of chlorine and bromine:

2,4,6-Trichloroaniline, m.p.  $78^\circ$ , b.p.  $262^\circ$  (*Wenghoff*, J. pr. **16**, 449; *Meyer*, Ber. **27**, 3151).

2,4,6-Tribromoaniline, m.p.  $119^\circ$  (*Gattermann*, Ber. **16**, 635).

3,4,5-Tribromoaniline, m.p.  $118\text{--}119^\circ$  (*Loring Jackson*, C. **1898**, I, 939).

2,4,6-Triiodoaniline, m.p.  $184^\circ$  (*Wheeler*, Am. Chem. J. **42**, 441).

Pentachloroaniline, m.p.  $232^\circ$ . Pentabromoaniline, m.p.  $262^\circ$ . Halogen compounds of benzene are produced by eliminating the amino-group by means of the diazo-reaction.

For di-, tri-, and tetra-iodoanilines and their transformation products see *Willgerodt*, Ber. **34**, 3343.

For further halogen derivatives of aniline see *Reed*, J. **91**, 1543; *Fries*, Ann. **346**, 160; for halogen alkylated anilines see *Braun*, Ber. **52**, 1716.

**NITRANILINES**,  $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2$ , are isomeric with phenylnitramine,  $\text{PhNHNO}_2$  (p. 111). Aniline is violently attacked by nitric acid and easily re-nitrifies.

1. Mono- and di-nitro compounds are obtained by nitration of acetanilide (p. 88). The amino-group is protected by the acetyl group, and the products first formed are *p*- and *o*-nitroacetanilides; with an excess of nitric acid the *p*-compound preponderates, but with equivalent of  $\text{HNO}_3$  dissolved in a mixture of glacial acetic acid and acetic anhydride, *o*-nitroacetanilide is the chief product (*Witt*, Ber. **39**, 3903). When aniline is nitrated in presence of conc. sulphuric acid in the cold, *m*-nitraniline is formed together with *o*- and *p*-nitranilines; the higher the concentration of sulphuric acid the greater the proportion of *m*-nitraniline (p. 101) (*Noelting*, Ber. **17**, 261; *Hübner*, Ber. **10**, 261). In concentrated sulphuric acid the amino-group is converted into the meta-directing  $-\text{NH}_2^+$  group (p. 15). The three isomers are separable owing to their different basicities; when their acidic solution is neutralised, *o*-nitraniline is precipitated first, then *p*-, and the *m*-last. Nitroacetanilides are separated similarly (*Witt*, Ber. **39**, 3903).

2. Nitranilines are obtained by heating halogen-nitrobenzenes with alcoholic ammonia at  $150\text{--}180^\circ$ , or heating nitrophenol ethers, such as  $\text{C}_6\text{H}_4(\text{NO}_2)\text{OC}_2\text{H}_5$ ,

with aqueous ammonia. Both methods succeed with para and ortho, but not with meta derivatives.

3. 2,4-Dinitranilines may be prepared by the direct introduction of an amino-group into meta-dinitro compounds by the action of alcoholic alkaline hydroxylamine solution (*Meisenheimer*, Ber. 39, 2533).

4. By partial reduction of polynitro-compounds (p. 72) (*Vesely*, Tchech. 1, 360).

5. By heating nitro-aminobenzene sulphonic acids with HCl to 170° (*Nietzki*, Ber. 18, 294) (Ger. Pat. 157,859), or with dilute H<sub>2</sub>SO<sub>4</sub> under reflux (*Ehrenfeld*, Org. Synth. 9, 64).

6. *o*- and *p*-Nitrانilines are formed by a rearrangement of phenylnitramine (*Orton*, J. 87, 389; *Bradfield*, J. 1929, 915).

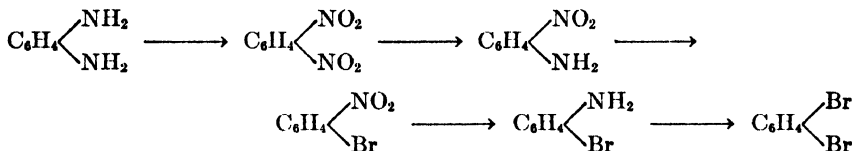
7. *o*-Nitrانiline is obtained by nitrating acetyl-sulphanilic acid (*Sakellarios*, Ber. 58, 2286).

1,2-, *o*-Nitrانiline, m.p. 71°; acetyl compound, m.p. 92°.

1,3-, *m*-Nitrانiline, m.p. 114°; acetyl compound, m.p. 155°.

1,4-, *p*-Nitrانiline, m.p. 147°; acetyl compound, m.p. 207°.

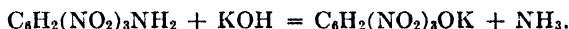
The nitrانilines link the diamino- and dinitro-benzenes to the nitro-halogeno-, amino-halogeno-, and dihalogeno-benzenes:



On boiling with alkali, the *o*- and *p*-nitrانilines (but not *m*-) lose NH<sub>3</sub> and give nitrophenols, C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)·OH; di- and tri-nitro-anilines react even more readily. With sodium and potassium alkylate in warm benzene, *p*-nitrانiline gives a coloured mono-potassium or mono-sodium salt, probably of quinonoid structure: NH·C<sub>6</sub>H<sub>4</sub>:NOOK (*Perkin*, J. 113, 508; *Green*, J. 113, 67).

The catalytic reduction of *p*-nitrانiline in the presence of aldehydes or ketones gives products substituted in both NH<sub>2</sub> groups; thus, with acetone, the reaction gives N,N'-diisopropyl-*p*-phenylene diamine. The other nitrانilines do not undergo this substitution (*Major*, Am. 53, 4373). *o*- and *m*-Nitrانiline give highly unstable N-dichloro-nitrانilines with HOCl (*Goldschmidt*, Ber. 55, 2450).

The similarity of the nitrانilines to the acid amides becomes closer as the number of nitro-groups in them increases; thus, picramide is hydrolyzed by caustic alkalis to picric acid and ammonia:



*o*-Nitrانiline derivatives of carbonic acid, viz., *o*-nitrophenylurea, m.p. 183°, *o*-nitrophenylguanidine, m.p. (+H<sub>2</sub>O) 53°, and *o*-nitrophenylthiourea, m.p. 136°, lose water on heating with dilute caustic alkalis, and the ring closes to form 1,2,4-benzo-triazine 1-oxides (*Arnold*, Ber. 46, 3522; 50, 1246).

From ammonia and the corresponding dinitro-phenols or polynitro-halogen-benzenes are obtained: 2,4-dinitraniline, m.p. 182°; 2,6-dinitraniline, m.p. 141-142°.

2,4,6-Trinitraniline, *picramide*, (NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NH<sub>2</sub>, orange coloured needles, m.p. 190°, has been obtained: 1. by nitrating aniline or acetanilide dissolved in conc. H<sub>2</sub>SO<sub>4</sub> in the absence of water (*Witt*, Ber. 41, 3091); 2. from picric acid *via* its ether, or by means of picryl chloride (p. 63), which latter reacts with aqueous NH<sub>3</sub> even in the cold; 3. by the action of an alkaline alcoholic solution of hydroxylamine on *sym*-trinitrobenzene (*Meisenheimer*, Ber. 39, 2539).

2,3,4,6-Tetranitrانiline, m.p. 220° (decomp.) and pentanitrانiline, m.p. 192° (decomp.), have been prepared by *Flurscheim* (Br. Pat. 243,079; J. 1928, 3041), the first by vigorously nitrating *m*-nitrانiline, the other from 3,5-dinitraniline by further nitration.

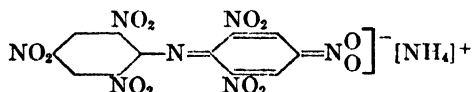
2,6-Dinitro-*p*-toluidine, m.p. 171°, 4,6-dinitro-*o*-toluidine, m.p. 135° have been obtained by partial electrolytic reduction of trinitro-toluene (*Brand*, Ber. 49, 673; *Körner*, Atti. R. Accad. Lincei 25, II, 339). The isomers can be separated by crystallisation from hot water.



*sym*-Trinitro-*m*-xylidine, m.p. 206°, is obtained from trinitro-chloroxylylene and ammonia (Klages, Ber. 28, 2047).

**NITRO-DIPHENYLAMINES** are obtained by acting upon nitro-halogen-benzenes with aniline, or nitranilines with bromobenzene in the presence of copper bronze or cuprous iodide (cf. p. 72). *o*-Nitro-bromobenzene, and polynitro-halogen-benzenes react with aniline even without a catalyst. Aryl-sulphonates of *o*-nitrophenol and its derivatives react similarly with aniline to form nitro-diphenylamines (Ullmann, Ber. 41, 1870). Numerous nitro-diphenylamines have also been prepared by nitrating nitroso- or benzoyl-diphenylamines, and hydrolysing the products with dilute sulphuric acid (Juillard, Bull. 33, 1172).

Nitro-diphenylamines are faintly yellow substances, forming dark red alkali salts whose stability increases with the number of nitro groups. Hexanitro-diphenylamine dissolves in aqueous alkalis with a purple colour. Its ammonium salt is a brick-red powder which was used as an orange dye for wool and silk, called *aurantia*, before the azo-dyes were known. It is used as a light filter in photography. The corresponding salt of pentanitro-diphenylamine is not a dye. The structure of these highly coloured alkaline salts is presumably quinonoid:



The nitro-diphenylamines would thus be classified as *pseudo*-acids (Vol. I, p. 50). Two series of alkyl derivatives are known: faintly yellow, stable N-ethers corresponding to the free nitro-diphenylamines, and dark-violet, unstable O-ethers corresponding to the dark alkaline salts, and sharing their quinonoid structure (*aci*-nitro derivatives).

- (I)  $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{NMeC}_6\text{H}_2(\text{NO}_2)_2$  (II)  $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{NHC}_6\text{H}_2(\text{NO}_2)_2\cdot\text{NOOMe}$   
pale yellow deep violet

*o*-, *m*-, and *p*-Nitro-diphenylamine,  $\text{NO}_2\text{C}_6\text{H}_4\text{NHC}_6\text{H}_5$ , m.p. 75°, 112°, and 133° (Lellmann, Ber. 15, 826; Schöpf, Ber. 22, 903; Goldberg, Ber. 40, 4545).

*o,o'*, *p,p'*, and *o,p'*-Dinitro-diphenylamine,  $\text{NO}_2\text{C}_6\text{H}_4\text{NHC}_6\text{H}_4\text{NO}_2$ , m.p. 167°, 216°, 222–223° (Bamberger, Ber. 31, 578).

2,4,6-Trinitro-diphenylamine, m.p. 179° is obtained from tetranitro-benzene or picryl chloride by the action of aniline (Margosches, Ber. 56, 1943). Trinitro-xylyl-phenylamine, m.p. 175° (Klages, Ber. 28, 2047). Other similar compounds, see Ber. 33, 504.

2,4,6,2',4'-Pentanitro-diphenylamine, m.p. 194°. Hexanitro-diphenylamine, *dipicrylamine*, m.p. 238° (decomp.), has been prepared from chlorobenzene and aniline by the action of  $\text{HNO}_3$  (Hoffmann, Am. 41, 1013).

N-Methyl-2,4-dinitro-diphenylamine,  $\text{PhNMeC}_6\text{H}_3(\text{NO}_2)_2$ , m.p. 167°, obtained from 1,2,4-chloro-dinitrobenzene and methylaniline, gives, on further nitration, N-methyl-hexanitro-diphenylamine (formula I above), m.p. 236°, yellow leaflets. The isomeric O-methyl-*aci*-hexanitro-diphenylamine (II), violet-black crystals decomposing at 141°, is obtained by the action of MeI on the silver salt of hexanitro-diphenylamine. The ester is rapidly hydrolysed by traces of alcoholic HCl. With acetyl chloride, on the other hand, the silver salt gives N-acetyl-hexanitro-diphenylamine, bright yellow crystals, m.p. 240° (Hamzsch, Ber. 41, 1747).

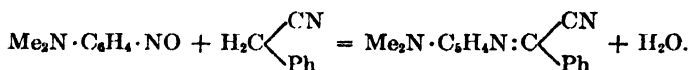
*o*-, *m*-, and *p*-Nitro-triphenylamine, m.p. 98°, 78°, and 144°, respectively, have been prepared by Piccard (Am. 39, 2006) by phenylating the three nitranilines. The *p*-isomer has also been obtained by Cambarjan (Ber. 41, 3510) from *p*-nitro-iodobenzene and diphenylamine by the addition of copper bronze. *p,p'*-Dinitro-triphenylamine, m.p. 196°.

**p-NITROSO-COMPOUNDS OF PRIMARY, SECONDARY, AND TERTIARY AROMATIC AMINES.** *Formation.*—1. When the nitrosamines of monomethylaniline or diphenylamine (p. 111) are treated with alcoholic HCl, they rearrange into *p*-nitroso-compounds (Fischer-Hepp rearrangement, Ber. 19, 2991).

2. Tertiary dialkyl-anilines react with nitrous acid, to yield *p*-nitroso-compounds (*Baeyer, Caro, Ber. 7, 963*). In this reaction nitro-compounds are formed as by-products (*Stoermer, Ber. 31, 2527*); *Hausermann, Ber. 32, 1912*). Ortho-substituents prevent the reaction (*Friedländer Mo. 19, 627*).

3. Nitroso-phenols fused with ammonium acetate and ammonium chloride give *p*-nitroso-anilines (*Mehne, Ber. 21, 429*).

*Behaviour*.—When heated with caustic soda the nitroso-compounds of secondary and tertiary aromatic amines break down into sodium nitroso-phenates and alkyl-amines. Tert.-nitroso-anilines condense with compounds containing reactive  $\text{CH}_2$ -groups; water is lost and compounds of the *azomethine* series are formed (*Ehrlich, Sachs, Ber. 32, 2341; 34, 118*), *e.g.*,



Important dyes of the *oxazine*, *thiazine*, and *induline* series are derived from tert-nitroso-anilines. For the dipole moments of some alkylated *p*-nitroso-anilines see *Le Fèvre, J. 1932, 39*.

*p*-Nitroso-aniline,  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , m.p.  $173^\circ$ , forms steel-blue needles (*Bamberger, Ber. 36, 3830*). *p*-Nitroso-monomethyl-aniline,  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NHMe}$ , m.p.  $118^\circ$ , forms blue lustrous flakes, freely soluble in dilute NaOH and precipitated from this solution by  $\text{CO}_2$ . Heated with aqueous NaOH it breaks up into methylamine and sodium-*p*-nitrosophenoxide. *p*-Nitroso-monoethyl-aniline, m.p.  $78^\circ$ .

*o*-, *m*-, and *p*-Nitroso-acetanilides,  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NHCOCH}_3$ , m.p.  $107^\circ$ ,  $111^\circ$ , and  $173^\circ$ , respectively, are obtained by the oxidation of the three monoacetyl-phenylene diamines with permonosulphuric acid. The *p*-isomer is known in a green and a colourless (dimeric) modification, m.p.  $173^\circ$  and  $181^\circ$ , respectively (*Cain, J. 93, 681*).

*p*-Nitroso-dimethylaniline,  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2$ , m.p.  $85^\circ$ , forms large green flakes. It is oxidised by potassium permanganate and potassium ferricyanide to *p*-nitro-dimethylaniline, whilst reducing agents convert it into amino-dimethylaniline, an important substance in the dye industry. It is decomposed by sodium hydroxide giving nitrosophenol and dimethylamine. Its hydrochloride is difficultly soluble. *p*-Nitroso-methyl-ethyl-aniline, hydrochloride, m.p.  $66-67^\circ$ , is obtained from methyl-ethyl-aniline by the action of  $\text{N}_2\text{O}_5$  (*Cain, Brit. Abstracts 1911, 437*). *p*-Nitroso-diethyl-aniline, m.p.  $84^\circ$ .

*p*-Nitroso-diphenylamine, m.p.  $144^\circ$ , forms green plates and is obtained from diphenyl-nitrosamine by the action of HCl gas. It dissolves in concentrated alkalis, and forms dark brown alkali salts which are derived from the anil of quinone-monoxime,  $\text{PhN} : \text{C}_6\text{H}_4 : \text{NOH}$  (*Fischer, Ber. 20, 1252; Ikata, Ber. 21, R227; Wieland, Ber. 39, 3039*).

*p*-Nitroso-triphenylamine, brown needles, m.p.  $120.5^\circ$ , is prepared by hydrolysing its hydrochloride, m.p.  $178^\circ$ , produced from triphenylamine by the action of amyl nitrite and HCl (*Piccard, Am. 40, 1074*).

#### 4. Diamines

Aromatic diamines, the amino groups of which are attached to the benzene ring, are obtained by the following methods:

1. Reduction of nitramines and dinitro-compounds, *e.g.*, with tin and hydrochloric acid.

2. Mono-amines are converted into amino-azo compounds (p. 138) and these are reduced:



3. Diamino-benzoic acids lose  $\text{CO}_2$  on heating with baryta; this reaction has proved of special importance in establishing the constitution of the three phenylene diamines (p. 11).

4. Phenylated diamino-benzenes are formed in the *semidine transformation* of hydrazobenzene (p. 145), e.g., *o*-amino-ditolyl-amine from hydrazotoluene.

5. Diphenylated diamino-benzenes,  $\text{C}_6\text{H}_4(\text{NHPh})_2$ , are formed when the dihydroxy-benzenes, resorcinol and hydroquinone (*q.v.*) are heated with aniline and  $\text{CaCl}_2$  or  $\text{ZnCl}_2$ .

**Properties.**—The diamines are colourless solids, volatilising without decomposition. They rapidly turn brown in the air. They are di-acid bases, and usually give salts which crystallise well. For the salts with organic acids see *Feigl*, Mo. 59, 136. In general the diamine adds on two equivalents of acid, whilst the other isomers add on only one. The coloration given by the solutions with ferric chloride is characteristic. Complex compounds are formed with certain metallic salts, e.g., the halides and sulphates of Co, Ni, Zn, Cd, and Cu (*Hieber*, Anorg. 180, 89). The hydrogen atoms of the amino-groups can be replaced in the same way as those of the monoamines.

**DIAMINO BENZENES, or PHENYLENE DIAMINES,  $\text{C}_6\text{H}_4(\text{NH}_2)_2$ .** The *o*-compound is prepared from *o*-nitraniline by reduction, best with zinc dust and  $\text{NaOH}$  (*Hinsberg*, Ber. 28, 2947). The *m*-compound is the most readily accessible. It is obtained from *m*-dinitrobenzene (p. 61). The *p*-compound is obtained by the decomposition of aminoazobenzene, by heating *p*-dichlorobenzene with ammonia in the presence of  $\text{CuSO}_4$  (Ger. Pat. 202,170), or by reducing *p*-nitraniline with Fe and HCl (*Jansen*, Z. Farbenind. 12, 197).

1,2- or *o*-Phenylene diamine, m.p.  $102^\circ$ , b.p.  $257^\circ$ .

1,3- or *m*-Phenylene diamine, m.p.  $63^\circ$ , b.p.  $287^\circ$ , dipole moment, 1.8.

1,4- or *p*-Phenylene diamine, m.p.  $147^\circ$ , b.p.  $267^\circ$ , dipole moment, 1.4–1.5.

For the acylation of *o*-diamines, see *Mason*, Ber. 47, 717; for diglycines of the three diamines see *Fraenkel*, Ber. 49, 485.

*o*-Phenylene diamine gives a dark-red colour with ferric chloride in hydrochloric acid solution, diamino-phenazine hydrochloride being formed. On oxidation with  $\text{PbO}_2$  or  $\text{Ag}_2\text{O}$  *o*-quinone-diimine is formed, which immediately polymerises to *o,o'*-diaminoazobenzene. In the table on p. 108 where the many condensations of *o*-diamines are shown, *o*-phenylene diamine may usually be taken as an example. Acetyl-*o*-phenylene diamine, m.p.  $132^\circ$  (*Leuchs*, Ber. 40, 1085). *o*-Amino-phenylurethane, m.p.  $86^\circ$ . *o*-Amino-dimethylaniline, b.p.  $217^\circ$  (*Bamberger*, Ber. 32, 1903). 4,6-Dinitro-*o*-phenylene diamine, m.p.  $215^\circ$ , forms dark red needles, and is obtained by the reduction of picramide with alcoholic ammonium sulphide (*Witt*, Ber. 41, 3093).

*m*-Phenylene diamine gives an intense yellow colour with even a very dilute solution of nitrous acid, due chiefly to the formation of 2,4,3'-triamino-azobenzene, and the disazo-compound,  $(\text{NH}_2)_2\text{C}_6\text{H}_3\text{:N:N:C}_6\text{H}_4\text{:N:N:C}_6\text{H}_3(\text{NH}_2)_2$ . This mixture is known as *Bismarck* or *Manchester brown*. Traces of nitrites or nitrous acid in water can thus be estimated colorimetrically (*Wislicenus*, Ber. 14, 1015). If the nitrite solution is added quickly to the hydrochloric acid solution of *m*-phenylene diamine, 1,2,4-nitroso-*m*-phenylene diamine,  $\text{NOC}_6\text{H}_3(\text{NH}_2)_2$ , garnet-red leaflets, m.p.  $210^\circ$  is formed in addition to the above-mentioned substances (*Bertels*, Ber. 37, 2276). For the action of  $\text{COCl}_2$ ,  $\text{CS}_2$ , and ethyl oxalate see *Gucci*, Ber. 21, R 521; *Koller*, Ber. 36, 411. Tetramethyl-*m*-phenylene diamine, b.p.  $267^\circ$  (*Pinnow*, Ber. 39, 3110). Tetraphenyl-*m*-phenylene diamine,  $\text{C}_6\text{H}_4(\text{NPh})_2$  is formed when *m*-dichlorobenzene is heated with potassium-diphenylamine (*Haüssermann*, Ber. 32, 1912). *o*-Nitro- and *o*-aminophenyl-*m*-phenylene diamine (Ger. Pat. 166,600). 2,4-Dinitro-*m*-phenylene diamine, m.p.  $254^\circ$  (*Meisenheimer*, Ber. 39, 2538).

*p*-Phenylene diamine is oxidised by the air to dark garnet-red crystals of

tetra-amino-diphenyl-*p*-azophenylene,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup [1]\text{N}[1]\text{C}_6\text{H}_3[2,5](\text{NH}_2)_2 \\ \diagdown [4]\text{N}[1]\text{C}_6\text{H}_3[2,5](\text{NH}_2)_2 \end{smallmatrix}$ , m.p.

231° (decomp.) (*Bandrowski*, Ber. 27, 480). It is oxidised by  $\text{Ag}_2\text{O}$  to quinone diimine (p. 242), by  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$  to quinone (p. 233), and by bleaching powder to quinone-dichlorimine (p. 244). For its poisonous effects see *Thompson*, Med. Rec., 97, 401. For detection with vanillic acid, see *Herold*, Seif.-Ztg. 61, 801. Acyl-*p*-phenylene diamines give acyl-*p*-phenylene-diazoimides,

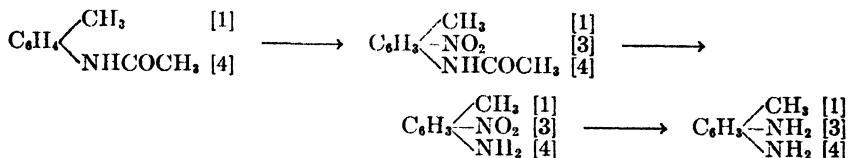
$\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{N} \cdot \text{CO} \cdot \text{R} \\ \diagdown \text{N}_2 \end{smallmatrix}$ , with liquid  $\text{N}_2\text{O}_3$  (*Morgan*, J. 111, 187). *p*-Amino-dimethyl-

aniline,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , m.p. 41°, b.p. 257°, is obtained by reduction of  $\gamma$ -nitroso- or *p*-nitro-dimethylaniline (p. 105) or by the decomposition of heliothine or of *p*-dimethylaminoazobenzene (*Fischer*, Ber. 16, 2235). With  $\text{H}_2\text{S}$  and  $\text{FeCl}_3$  in acid solution it gives a dark-blue colour, due to methylene blue, and is used as a sensitive reagent for the detection of hydrogen sulphide. *N,N'*-Dimethyl-*p*-phenylene diamine,  $\text{CH}_3\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHCH}_3$ , m.p. 53°, b.p. (17 mm.) 150°, is oxidised to quinone-dimethylhydrazine by  $\text{Ag}_2\text{O}$  (*Willstätter*, Ber. 38, 2243). Thionyl- and formyl-*p*-aminodimethylaniline (*Pinnow*, Ber. 27, 602). Nitro-*p*-phenylene-diamine, m.p. 135°, lustrous green needles, is obtained from 1,2,4-dinitraniline (*Kehrmann*, Ber. 28, 1707; *Bülow*, Ber. 29, 2287).

**DIAMINOTOLUENES, TOLUYLENE-DIAMINES.** All six isomers are known.

1. 2,3-Toluylene-diamine, m.p. 61°, b.p. 255° (*Lellmann*, Ann. 228, 243).
2. 2,4-Toluylene-diamine, m.p. 99°, b.p. 280°.
3. 2,5-Toluylene-diamine, m.p. 64°, b.p. 273°.
4. 2,6-Toluylene-diamine, 105°.
5. 3,4-Toluylene-diamine, m.p. 89°, b.p. 265°.
6. 3,5-Toluylene-diamine, m.p. liquid, b.p. 284° (*Stadel*, Ann. 217, 200).

3,4-Toluylene-diamine is the most accessible *o*-diamine; it is prepared from acetyl-*p*-toluidine:



2,4-Toluylene-diamine is the starting material for the manufacture of toluylene red (Vol. IV).

**XYLYLENE DIAMINES.** All the eleven possible diamino-xylenes or xylylene-diamines have been prepared. Four are derived from *o*-phenylene diamine:  $(\text{NH}_2)_2[1,2]\text{Me}_2[3,4]$ , m.p. 89°;  $-\text{[4,5]}$ -, m.p. 126°;  $-\text{[3,5]}$ -, m.p. 78°;  $-\text{[3,6]}$ -, m.p. 75°. Four are derived from *m*-phenylene diamine:  $(\text{NH}_2)_2[1,3]\text{Me}_2[4,5]$ , m.p. 67°;  $-\text{[2,4]}$ -, m.p. 66°;  $-\text{[4,6]}$ -, m.p. 105°;  $-\text{[2,5]}$ -, m.p. 103° (*Noelling*, Ber. 35, 636); and three from *p*-phenylene diamine:  $(\text{NH}_2)_2[1,4]\text{Me}_2[2,3]$ , m.p. 116°;  $-\text{[2,6]}$ -, m.p. 104°;  $-\text{[2,5]}$ -, m.p. 150°.

1,2,3,5,6-, *o*-Diaminopseudocumene, m.p. 90°. 1,4,3,5,6-*p*-diaminopseudocumene, m.p. 78° (*Bamberger*, Ber. 24, 1647). Diaminomesitylene, m.p. 90° (*Ladenburg*, Ann. 179, 176), etc.

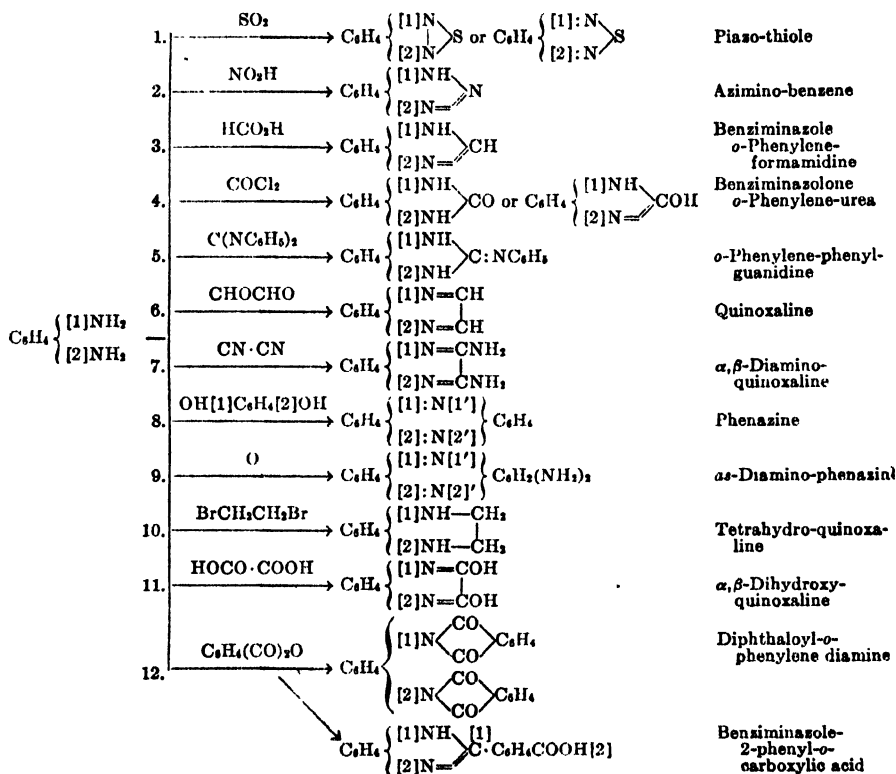
In the toluylene-diamines an  $\text{NH}_2$  group in the *p*-position to methyl is more easily acylated than an  $\text{NH}_2$  group in the *o*- or *m*-positions (*Bülow*, Ber. 35, 681). For the influence of a nuclear methyl group on the *N*-alkylation of phenylene-diamines, see *Morgan*, Proc. 18, 87).

*o*-Amino-diphenylamine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NHC}_6\text{H}_5$ , m.p. 79°, is obtained from *o*-nitro-diphenylamine with  $(\text{NH}_4)_2\text{S}$ , and *p*-amino-diphenylamine, m.p. 75°, similarly from *p*-nitroso-diphenylamine. The *p*-compound is also formed in the electrolytic reduction of nitrobenzene in hydrofluosilicic acid solution. Ferric chloride oxidises it to emeraldin (p. 246) (*Nover*, Ber. 40, 289). *p,p'*-Diamino-diphenylamine, m.p. 158°, is formed in the semidine rearrangement of *p*-amino-hydrazobenzene (*Barbier*, Bull. [3], 33, 1232).

*p*-Amino-triphenylamine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{C}_6\text{H}_5)_2$ , m.p. 145–148°, is formed by the reduction of the corresponding nitro-compound. A *p*-chloro-anilino-triphenylamine,  $\text{ClC}_6\text{H}_4\text{NHC}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)_2$ , m.p. 77–81°, is the product of a complicated series of reactions occurring when tetraphenyl-hydrazine (p. 149) is decomposed with hydrochloric acid (Gambarjan, Ber. 41, 3507).

### Condensation of the *o*-Diamines

The *o*-diamines easily form condensation products which usually contain ring-systems of 5 or 6 atoms, and which will be dealt with in Vol. IV as *heterocyclic* compounds. Neither the *m*- nor the *p*-diamines possess this power. The condensations involve the replacement of hydrogen atoms in both amino groups by a polyvalent atom or group of atoms.



1. By the action of  $\text{SO}_2$  and  $\text{SeO}_2$ , *piazo-thioles* and *piazo-selenoles* respectively are formed.

2. With  $\text{HNO}_2$ , *azimino-benzenes* are obtained.

3. Carboxylic acids and their chlorides and anhydrides, and aldehydes give *cyclic amidines* with *o*-diamines. These *anhydro-bases* and *aldehydines* (Ladenburg) are closely related to the *glyoxalines* and *iminazoles*. Such condensations have also been observed in the reduction of acylated *o*-nitramino compounds (Hobbecker).

4. *Cyclic derivatives of urea and thiourea* are formed by the action of  $\text{COCl}_2$ ,  $\text{CS}_2$ , or by condensation of urea, thiourea, or ammonium thiocyanate (p. 121).

5. *Cyclic guanidine derivatives* are obtained by the action of carbodiimides (p. 99) and phenyl mustard oils (p. 98).

6. A remarkable reaction of the *o*-diamines is that with glyoxal and other  $\alpha$ -dicarbonyl compounds, and also with glucose, in which the so-called *quinoxalines* are formed with loss of water (*Hinsberg*).

Six-membered rings similar to that formed in the last-named reaction are obtained by: 7. The condensation of *o*-diamines with cyanogen; 8. condensation with dihydroxy-benzenes; 9. oxidation of *o*-phenylene diamine which gives *as-diaminophenazine*. 10. *o*-Phenylene diamine dibenzene sulphonates condense with alkylene dihalides, such as  $\text{CH}_2\text{I}_2$ ,  $\text{C}_2\text{H}_4\text{Br}_2$ , and trimethylene bromide, to form cyclic diamines, which lose the benzene sulphonic groups and give the corresponding *phenylene-alkylene-diamines* (*Hinsberg*, Ber. 28, R 756). 11. Other heterocyclic rings are formed by condensation with oxalic acid and homologous aliphatic dicarboxylic acids, and with phthalic acid (*Meyer*, Ann. 327, 9). 12. *o*-Phenylene diamine and phthalic anhydride condense on boiling to form diphthaloyl-*o*-phenylene diamine and benzimidazole-2-phenyl-*o*-carboxylic acid (*Lieb*, Mo. 39, 873).

The aminophenols, *o*-aminothiophenols, and *o*-dihydric phenols undergo similar condensations to those of the *o*-diamines.

### Differences between the *o*-, *m*-, and *p*-Diamines

1. The *p*-diamines take part in the formation of dyestuffs of various classes. When a mixture of a *p*-diamine with a primary amine, or a phenol, is oxidised in a suitable manner at ordinary temperature, *indamine* and *indophenol* dyes, respectively, are formed; at higher temperatures *safranine* dyes are produced (Vol. IV). When *p*-diamines containing a free amino group are oxidised with ferric chloride in the presence of  $\text{H}_2\text{S}$ , sulphur-containing dyes of the thiodiphenylamine series are formed (*Lauth's* dyes). On oxidation with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$ , the *p*-diamines give quinones, which are easily recognised by their smells. For the colour reaction with ferric chloride see *o*-phenylene diamine above.

2. *o*-Diamines form *azimino*-compounds with nitrous acid (see above). *m*-Diamines, on the other hand, give brown aminoazo-dyes (see *phenylene brown*, p. 143). This is used as a test for nitrous acid (*Griess*, Ber. 11, 624, 627). With excess of nitrous acid and in acid solution both *m*- and *p*-diamines form *bis-diazo* compounds.

3. When heated with ammonium thiocyanate the hydrochlorides of the diamines give dithiocyanates, e.g.,  $\text{C}_6\text{H}_4(\text{NH}_2\text{HSCN})_2$ . When heated to  $120^\circ$  the thiocyanates of *o*-diamines are converted into cyclic thioureas, e.g.,  $\text{C}_6\text{H}_4(\text{NH})_2\text{CS}$ ; the sulphur is not removed from these compounds by warming with an alkaline solution of a lead salt. The compounds obtained from *m*- and *p*-diamines, on the other hand, give an immediate black colour with such a solution (*Lellmann's* reaction, Ber. 18, R 326).

4. The diamines give dithio-ureas with mustard oils. If these products are fused, the *o*-derivatives decompose into cyclic phenylene-thioureas and dialkylthioureas, and the melt soon becomes solid. Compounds derived from *m*-diamines melt without decomposition, and those from *p*-diamines are completely broken down (*Lellmann*, Ber. 18, R 327; 19, 808).

5. The *o*-diamines undergo a number of condensation reactions which are given above, and by which they can be distinguished from *m*- and *p*-diamines. The *o*-diamines are detected by their behaviour towards *phenanthraquinone* (q.v.). The reaction with *croconic acid* is even more sensitive (*Nietzki*, Ber. 19, 2727). Quinoxaline derivatives are formed in both these reactions.

**TRIAMINES.** The three possible triaminobenzenes are known, though the symmetrical compound has only been obtained in the form of its salts. 1,2,3-Triaminobenzene, m.p.  $103^\circ$ , b.p.  $336^\circ$  (*Salkowski*, Ann. 163, 23), is obtained from triaminobenzoic acid, the reduction product of chrysanic acid. 1,2,4-Triaminobenzene, m.p. below  $100^\circ$ , b.p.  $340^\circ$  is obtained from chrysoidin (*Witt*, Ber. 10, 659; *Griess*, Ber. 15, 2196) or diamir zobenzene (p. 142), and from the corresponding nitro-amino compounds (*Hinsberg*, Ber. 19, 1253). On oxidation in the air it is converted into a eurhodine *u*, *uller*, Ber. 22, 856). 2,3,4-Triaminotoluene (*Ruhemann*, Ber. 14, 2657).

**2,4,6-Triaminotoluene**, m.p. 121°, is obtained from 2,4,6-trinitrotoluene by catalytic reduction (*Hein, Wagner*, Ber. 68, 856). **Triaminomesitylene**, m.p. 118–119°, see *Morgan*, J. 123, 228. Di-, tetra-, and hexamethylated triamines, see *Pinnow*, Ber. 29, 1053; 30, 3110.

**TETRAMINES.** *v-* or 1,2,3,4-Tetra-aminobenzene is obtained from diquinoyltetroxime by reduction (*Nietzki*, Ber. 22, 1649). *sym-* or 1,2,4,5-Tetra-aminobenzene, obtained from dinitro-*m*-phenylene diamine, shows the reactions of *o*- and *p*-diamines (*Nietzki*, Ber. 22, 440). *as-* or 1,2,3,5-Tetra-aminobenzene, is obtained from tetranitrobenzene (*Nietzki*, Ber. 34, 57), and from picryl-hydroxylamine by reduction with stannous chloride and HCl. *Tetra-acetyl compound*, m.p. 245° (*Borsche*, Ber. 56, 1942).

**PENTAMINES.** Pentaminobenzene is obtained from trinitro-*m*-phenylene diamine. Pentaminotoluene,  $\text{CH}_3\text{C}_6\text{(NH}_2)_5$ , is obtained from trinitro-*sym*-toluylene diamine (*Palmer*, Ber. 26, 2304).

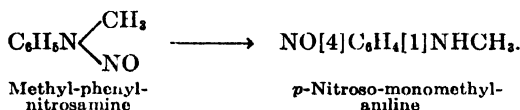
**HEXAMINES.** Hexaminobenzene, m.p. 247–248° (decomp.) forms brown octahedra, and is produced by the reduction of trinitro-triamino-benzene with phenylhydrazine (*Flurscheim*, J. 1929, 330).

As the number of amino-groups increases the polyamines become less stable and more readily oxidised.

In the *sym*-triaminobenzenes the  $\text{NH}_2$  groups can be replaced by OH by heating with HCl. In this way phloroglucinol is formed from *sym*-triaminobenzene (*Weidel*, Mo. 21, 20; *Wenzel*, Mo. 22, 983).

### (f) Phenyl-nitrosamines

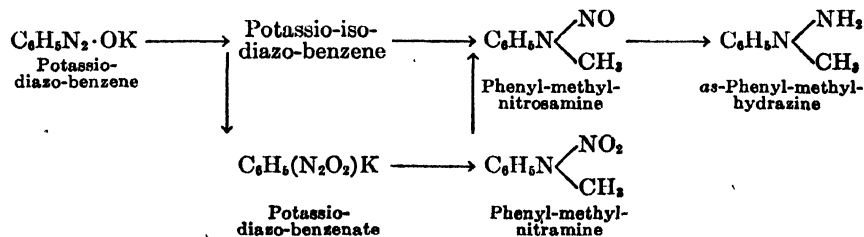
Aromatic nitrosamines are obtained in the same way as aliphatic nitrosamines, by the action of potassium nitrite on the hydrochlorides of secondary amines. This reaction may be used to distinguish between and separate the secondary amines and the primary and tertiary amines, since the nitrosamines can be precipitated as oils from the acid solution of a mixture of bases. The phenylnitrosamines are converted into *p*-nitrosoanilines by the action of gaseous HCl on their alcoholic or ethereal solutions (p. 104):



For the rearrangement of nitrosamines into *p*-nitrosoanilines see *Henrich*, Theorie der organ. Chemie, 5th. ed., p. 432.

They give hydrazines on reduction, or break down into ammonia and the original secondary bases. For the catalytic reduction of the nitrosamines, see *Paal*, Ber. 63, 57. They are volatile in steam (*Hepp*, Ber. 10, 329; *Reverdin*, Ber. 22, 1006; *Fischer*, Ann. 190, 151). They decompose, however, on dry distillation.

The nitrosamines bear a close relationship to the diazo-compounds as well as to the secondary amines and the hydrazines. Potassium benzene-diazotate (p. 120) will isomerise to potassium benzene-isodiazotate, which gives phenyl-methyl-



nitrosamine with methyl iodide. This compound gives *as*-phenyl-methyl-hydrazine on reduction. Potassium benzene-isodiazotate gives the potassium salt of nitranilide on oxidation. This gives phenyl-methyl-nitramine on treatment with methyl iodide, which can be reduced to phenyl-methyl-nitrosamine and *as*-phenyl-methyl-hydrazine. These constitutional relationships are shown in the scheme on the preceding page.

**Phenyl-methyl-nitrosamine**,  $C_6H_5N(CH_3)NO$ , m.p. 12–15° (*Bamberger*, Ber. 27, 365, footnote) is obtained from nitroso-phenylglycine,  $C_6H_5N(NO)CH_2COOH$  by boiling with water (*Fischer*, Ber. 32, 247). The methyl group is split off on fusion with potash, and potassium benzene-isodiazotate is formed (p. 120). In the cold, phenyl-methyl-nitrosamine in aqueous, alcoholic, or acetic acid solution, forms a hydrochloride with HCl,  $[C_6H_5N(NO)CH_3]HCl$  (an analogous hydrobromide is formed with HBr: *Fischer*, Ber. 45, 1098). On boiling or heating it is converted into the isomeric *p*-nitroso-methylaniline (*Hantzsch*, Ber. 35, 2975). **Phenyl-ethyl-nitrosamine**,  $C_6H_5N(C_2H_5)NO$ , is a yellow oil, smelling of bitter almonds (*Griess*, Ber. 7, 218). **Phenyl-*n*-butyl-nitrosamine**, is a bright-yellow oil, volatile with steam. It is reduced by zinc dust in a mixed solvent of acetic acid and alcohol to phenyl-*n*-butyl-hydrazine (*Reilly, Hickinbottom*, J. 111, 1026). **Diphenyl-nitrosamine**,  $(C_6H_5)_2NNO$ , m.p. 67°, forms pale-yellow plates. It dissolves in conc.  $H_2SO_4$  with a dark blue colour, and its solution in benzene loses NO on heating. In alcoholic solution it is exceedingly readily hydrolysed by traces of mineral acids (*Marqueyrol*, Bull. 11, 804; 15, 510). For further aromatic nitrosamines see *Bamberger*, Ber. 33, 100.

**NITROSOANILIDES**. These substances are more closely related to the diazo-compounds even than the phenyl-alkyl-nitrosamines. They are obtained (1) by the action of nitrous acid on the acetic acid solution of anilides, and (2) from *n*- or *iso*-alkali diazotates in alkaline solution by the action of acid chlorides. They are broken down again into anilides and nitrosyl chloride, NOCl, by the action of HCl gas, and on reduction the anilides are always regenerated. With alkalis, on the other hand, the acyl-group is removed, even in the cold, and alkali diazotates are formed. With potassium sulphite, nitroso-acetanilide gives benzene diazo-sulphonic acid, and phenyl-hydrazine disulphonic acids. With benzene it gives nitrogen and diphenyl (*Bamberger*, Ber. 30, 366; *Hantzsch*, Ann. 325, 226). **Nitroso-acetanilide**,  $C_6H_5N(NO)COCH_3$ , m.p. 40°. **Nitroso-formanilide**,  $C_6H_5N(NO)CHO$ , m.p. 39°. ***p*-Bromo-nitroso-acetanilide**, yellow needles, exploding at 88°. **Nitroso-diphenylurea**,  $C_6H_5N(NO) \cdot CO \cdot NHC_6H_5$ , m.p. 82° (decomp.), reacts like nitrosoanilides.

### (g) Phenyl-nitramines\*

**Nitranilide**, *phenyl-nitramine*, *phenyldiazotic acid*,  $C_6H_5NH \cdot NO_2$  or  $C_6H_5N:-NOOH$  (for the formula  $C_6H_5N(O):NOH$ , see *Hantzsch*, Ber. 64, 656), m.p. 46°, forms colourless crystals. It is obtained: 1. By oxidation of potassium benzene-*n*-diazotate or -*iso*-diazotate with potassium ferricyanide or potassium permanganate (Ger. Pat. 77,397), when it is formed together with the isomeric nitroso-phenyl-hydroxylamine,  $C_6H_5N(NO)OH$  (*Bamberger*, Ber. 42, 3568). 2. By nitrating aniline with nitrogen pentoxide (*Bamberger*, Ber. 27, 585, cf. *Romburgh*, Ber. 29, 1015; *Hoff*, Ann. 311, 91), or with nitric acid in acetic acid solution, or with  $KOC_2H_5$  and ethyl nitrate (*Angeli, Atti. Accad. Lincei* 14, [1], 127). 3. By the action of sodium or  $KOC_2H_5$  on an ethereal solution of aniline and ethyl nitrate (*Bamberger*, Ber. 53, 2321). 4. By the decomposition of diazo-benzene perbromide with alkalis, when nitrosobenzene is also formed (*Bamberger*, Ber. 27, 1273; Ger. Pat. 77,264). 5. By the action of nitryl chloride on aniline (*Bamberger*, Ber. 27, 668). 6. From aniline nitrate by removal of water by means of acetic anhydride, in the same way as acetanilide is obtained from aniline acetate (*Hoff*, Ann. 311, 99). Nitramines are also obtained from *sym*-diazotates by the action of caustic alkalis in the cold (Br. Pat. 307,965). The presence of a nitro-group in the *m*-position facilitates the formation of nitramine (U. S. Pat. 1,752,998; *Macciotta, Gazz.* 60, 408). Methods 1 and 6 have been used for preparing a number of substituted nitramines.

\* *H. J. Becker*, Die Nitramine, Stuttgart, 1912.



**Properties and reactions.**—Nitramine isomerises in the light, on heating, or in the presence of mineral acids, forming a mixture of *o*- and *p*-nitranilines. It is probable that nitramine is an intermediate product in the nitration of aniline. When reduced with sodium amalgam it forms sodium *iso*-diazotate, which is then further reduced to phenylhydrazine (*Bamberger*, *Ber.* 27, 1181). With zinc and acetic acid it forms a diazonium salt,  $C_6H_5N_2O_2K$ , and its sodium salt form shining white leaflets. The formula  $C_6H_5N:N(O)OH$  is assigned to the salts, but the free acid is  $C_6H_5NH.NO_2$  (*Hantzsch*, *Ber.* 64, 656). With nitric acid it forms phenyl-diazonium nitrate. Its  $\alpha$ -methyl ester, phenyl-

methyl-nitramine,  $PhN \begin{smallmatrix} \swarrow Me \\ \searrow NO_2 \end{smallmatrix}$ , is obtained by the action of methyl iodide on the

sodium salt. It melts at  $39^\circ$  and rearranges into *o*- and *p*-nitromethylanilines in the presence of  $H_2SO_4$ . When heated with caustic potash it gives methyl-aniline, and on reduction gives methyl-phenyl-nitrosamine, *as*-methyl-phenylhydrazine and monomethylaniline. The silver salt gives methyl  $\beta$ -diazobenzenate,  $PhN:NOOCH_3$ , a yellowish-brown oil smelling of heliotrope, with methyl iodide (*Bamberger*, *Ber.* 27, 359; *Hantzsch*, *Ber.* 31, 177; *Bamberger*, *Ber.* 31, 574). For the action of  $H_2SO_4$  on substituted nitramines see *Reverdin*, *Bull.* 11, 485; for the nitration of nitramines see *Macciotta*, *Gazz.* 61, 773, 777.

**HOMOLOGOUS NITRAMINES.** The *sym*-trisubstituted phenyl-nitramines in which the positions *o*- and *p*- to the amino-group are occupied do not undergo the rearrangement to nitranilines. They are unaffected by mineral acids, and are obtained from the corresponding anilines by direct nitration with  $HNO_3$ .

*o*-Benzyl-nitramine is a colourless oil. *p*-Benzyl-nitramine, m.p.  $52^\circ$ . Pseudocumeryl-nitramine, m.p.  $87^\circ$ . *o*-, *m*-, *p*-Nitrophenyl-nitramine, m.p.  $65^\circ$ ,  $92^\circ$ , and  $111^\circ$ , respectively (*Bamberger*, *Ber.* 28, 399). 3,5-Dinitro-*p*-tolylmethyl-nitramine,  $(NO_2)_2C_6H_3(CH_3).N(CH_3)NO_2$ , m.p.  $138^\circ$ , is obtained by the action of nitric acid on dimethyl-*p*-toluidine (*Romburgh*, *Ber.* 29, 1015). Nitro-m-xylol-nitramine, m.p.  $90-91^\circ$  is obtained by the action of potassium ferricyanide on the potassium isodiazotate of 1-nitro-3,5-xylidine (*Bamberger*, *Ber.* 53, 2321).

2,4,6-Trichloro-phenyl-nitramine, m.p.  $135^\circ$ . 2,4,6-Tribromo-phenyl-nitramine, m.p.  $144^\circ$  (*Orton*, *Proc.* 21, 91). 2,4-Dinitro-phenyl-nitramine, m.p.  $101^\circ$  (decomp.) is obtained by the action of conc. nitric acid on *o*- and *p*-nitraniline or 2,4-dinitraniline (*Zincke*, *Ann.* 339, 229). 2,4,6-Trinitro-phenyl-nitramine, m.p.  $208-215^\circ$ , is highly explosive, and is obtained as a by-product in the nitration of aniline (*Witt*, *Ber.* 41, 3094; 42, 2959). For the reaction of this compound with bases see *van Duin*, *Rec.* 38, 89. 2,4,6-Trinitrophenyl-methyl-nitramine, an explosive known under the name of *tetryl*, m.p.  $125-130^\circ$ , is obtained by the nitration of mono- or di-methylaniline (*Davis*, *Am.* 46, 1063).

### (h) Diazo-compounds\*

The aromatic diazo-compounds, because of their ready conversion into the most diverse substitution products of the aromatic hydrocarbons, and as intermediate steps in the formation of azo-dyes, are equally important both from a scientific and an industrial standpoint.

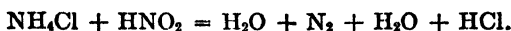
The term "aromatic diazo-compounds" comprises three constitutionally different, but readily interconvertible classes of substances; the diazonium salts, the diazo-hydrates, and the metallic salts of the latter, or diazotates.

#### 1. Diazonium Salts

The behaviour of the primary aliphatic amines towards nitrous acid was particularly pointed out in Vol. I (p. 194). The amino-group can by this means be replaced by hydroxyl. The reaction

\* *K. H. Saunders*, *The Aromatic Diazo-compounds*, London, 1936.

corresponds to that of ammonia with nitrous acid, which gives nitrogen and water:



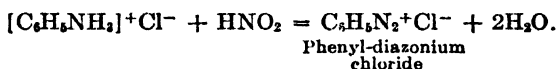
An exception to this reaction was mentioned (Vol. I, p. 458): those aliphatic amines, in which the carbon attached to the amino-group is also attached to an acid radical such as COOR, CN, COR, form aliphatic diazo-compounds on treating their salts with nitrous acid in a not too strongly acid medium. Ethyl aminoacetate, for example, gives diazoacetic ester:



An analogous reaction, which occurs in the moderated action of nitrous acid on the salts of primary aromatic amines, had been observed much earlier. If nitrous acid is allowed to act upon these salts without cooling, the result is the same as with aliphatic amines, the amino-group being replaced by hydroxyl:



In the cold, however, no nitrogen is given off, but three hydrogen atoms of the cation are replaced by one nitrogen atom, and a diazonium salt is formed:



Most of these diazonium salts are readily soluble in water, and therefore remain in solution as ions, the anions being  $\text{Cl}^-$ ,  $\text{HSO}_4^-$ ,  $\text{NO}_3^-$ , etc., according to the amine salt used. If the solution is heated, nitrogen is evolved and one hydroxyl group replaces the nitrogen given off, converting the diazonium salt into the electrically neutral phenol:

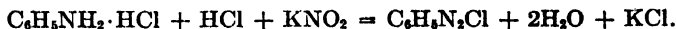


The aromatic diazonium salts differ from the aliphatic diazo-compounds in the fact that in the former the group  $\text{RN}_2$  is a cation containing the unchanged aryl group, e.g., Ph, of the amine used, while in the formation of the aliphatic diazo-compounds, the carbon atom to which the  $\text{NH}_2$  group was attached loses a H atom. This hydrogen is not a neutral atom, but a hydrogen nucleus (proton), which takes the positive charge with it, and leaves an electrically neutral molecule, such, for example, as diazo-acetic ester.

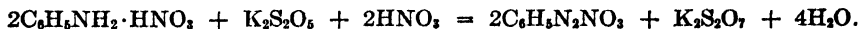
*Methods of formation of the diazonium salts.*—(1a) Nitrous fumes, prepared by heating arsenous oxide with nitric acid, are passed into an aqueous paste of the salt to be diazotised. The mixture is cooled with ice. The diazonium salt is precipitated from solution by a mixture of alcohol and ether.

(1b) To the cooled solution of the salt to be diazotised a quantity of acid equivalent to the amount of  $\text{KNO}_2$  or  $\text{NaNO}_2$  to be used is

added, followed by the nitrite itself. The mixture must be efficiently cooled.



(1c) Feebly basic amines, such as dinitraniline, which do not form salts in aqueous solution, are dissolved in conc.  $\text{HNO}_3$ , and the necessary amount of potassium metabisulphite to effect the reduction of the nitric acid to nitrous acid is added (*Witt*, Ber. 42, 2956):



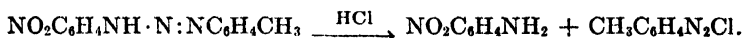
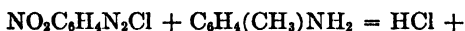
The amine may also be dissolved in conc.  $\text{H}_2\text{SO}_4$  and solid  $\text{NaNO}_2$  added. This really means that the diazotisation is effected with nitrosylsulphuric acid (*Claus*, J. pr. 56, 48; cf. Ann. 266, 224). In many cases diazotisation can be carried out with advantage by the action of nitrosylsulphuric acid on the amine in acetic acid solution.

In other cases, e.g., in the diazotisation of the mono-nitranilines, the substance may be dissolved in concentrated acid, diluted with water, and nitrite solution allowed to trickle in to the cooled liquid, regardless of the free amine separating out by hydrolysis. The amine re-dissolves as a diazonium salt. Even those amines which are very feeble bases and are easily liberated by hydrolysis from their salts, form diazonium salts which are not hydrolysed at all, because they are quaternary salts.

2. Since the diazonium salts are much more soluble in water than in alcohol, the solid salts are prepared with advantage in alcoholic or acetic acid solution using alkyl nitrites as the diazotising agents (*Hantzsch*, Ber. 34, 3338).

Industrially some other methods are used to obtain solid diazonium salts (see, for example, Ger. Pats. 94,495 and 94,948).

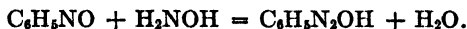
Sometimes the diazo-group migrates in a peculiar way when solutions of diazonium and aniline salts are mixed. Thus, nitro-phenyl-diazonium chloride and toluidine rearrange to give toluene-diazonium chloride and nitraniline (*Schraube*, Ber. 29, 287). This occurs presumably *via* an intermediate diazoamino compound:



3. The nitrate of an amine is reduced with zinc dust and HCl (Ger. Pat. 25,146).



4. By the action of hydroxylamine on nitrosobenzenes:



5. When nitric oxide is passed through a chloroform solution of nitrosobenzene, phenyl-diazonium nitrate separates out (*Bamberger*, Ber. 30, 512).



6. By the hydrolysis of nitroso-acetanilide by means of caustic potash.

7. By the action of sodamide on nitrobenzene (*Bamberger*, Ber. 37, 629).

8. By the action of caustic soda on a mixture of phenylhydroxylamine and benzene-sulphohydroxamic acid (*Angeli*, Ber. 37, 2390).



9. Salts of phenylhydrazine are treated with  $\text{HgO}$ , or the free phenylhydrazines in alcoholic solution are treated with chlorine or bromine at a low temperature. This is a useful method for the preparation of solid diazonium salts (p. 116).

10. Thionyl-phenylhydrazine (p. 154) is treated with thionyl chloride, acetyl chloride, or other acid chlorides (*Michaelis*, *Ann.* 270, 116).



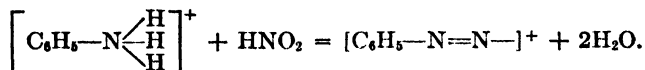
**Properties.**—The aromatic diazonium salts are usually crystalline, colourless substances, which turn brown in the air. For the effect of light see *Schmidt*, *J. pr.* 132, 153. They are readily soluble in water, sparingly in alcohol, and are precipitated from their alcoholic solutions by the addition of ether. For electrical conductivity and cryoscopy see *Goldschmidt*, *Ber.* 28, 1734, 2020. They are, in general, very unstable (*Hirsch*, *Ber.* 24, 324), and decompose with explosive violence when heated or struck. Stable diazonium-compounds are obtained by precipitation by salts of aromatic polysulphonic acids in the presence of salts of metals of Group II in the periodic system (*Fr. Pat.* 697,425). Diazonium salts are very reactive, and can react readily and smoothly in a great diversity of ways. They can be reduced to hydrazines, or oxidised to nitramines, the nitrogen being retained in the molecule, or the azo-nitrogen can be split off, and the diazo-group can be directly replaced by hydrogen, halogens, hydroxyl, and other groups.

**History and constitution.**—The diazo-compounds were discovered at the close of the 1850's by *Griess* (*Ann.* 137, 39). He regarded them as addition products of  $\text{C}_6\text{H}_5\text{N}_2$  and acids such as  $\text{HCl}$ . *Kekulé* (*Z. Chem.* [N.F.] 1866, 2, 308; *Chemie der Benzolderivative*, 1, 223) proved that the  $\text{N}_2$  group replaces only one hydrogen atom in benzene, so that the chloride is not  $\text{C}_6\text{H}_5\text{N}_2\text{HCl}$  but  $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ . This was clearly established by *Limpricht's* discovery (*Ber.* 10, 1537) of diazonium salts and betaines formed from aniline salts in which the five remaining hydrogen atoms are replaced, *e.g.*, tetrabromo-sulphanilic acid. *Kekulé* formulated phenyldiazonium chloride as  $\text{C}_6\text{H}_5\text{—N=N—Cl}$ , but *Blomstrand* (1896), *Strecker*, and *Erlenmeyer, Sr.*, regarded it as an ammonium salt, writing it as  $\text{Ph—N}\equiv\text{N}^+$  with penta-

valent nitrogen, according to the theory then prevailing. Since then these salts have been referred to as "diazonium salts" instead of the earlier term "diazo-benzene chloride" or "acid salts of diazo compounds."

At present the diazonium salts are formulated after *Blomstrand*, as ionic compounds:  $[\text{R}\cdot\text{NN}]^+\text{Cl}^-$ . The formerly controversial question as to which of the two nitrogen atoms the acid residue is linked thus becomes irrelevant. The diazonium salts are thus regarded as salts of a univalent positive ion. In favour of this view *Hantzsch*, in particular, has put forward many arguments. Solubility, cryoscopic behaviour and conductivity of the solutions, stability in water while the salt of the corresponding amine is hydrolysed, the fact that the perchlorates are sparingly soluble like those of potassium and ammonium, and the tendency of diazonium halides to attach free halogen molecules to the halogen ion, forming sparingly soluble crystalline perhalides, *e.g.*, phenyldiazonium perbromide  $[\text{C}_6\text{H}_5\text{N}_2]^+\text{Br}^-\text{Br}_2$ , are in favour of this structure. The stable crystalline perhalides are characteristic of bulky cations such as rubidium and caesium, and tetra-alkyl-ammonium (*Hantzsch*, *Ber.* 28, 1734; 32, 3135; 48, 1344).

The transformation by nitrous acid of aryl-ammonium salts into diazonium salts may be regarded as a simple replacement within the cation of three protons by one  $\text{N}^{+++}$  from the nitrous acid, the anion not taking part at all:



Since  $\text{N}^{+++}$  denotes a nitrogen atom which has lost three of its five valency electrons, the  $\beta$ -nitrogen of the diazonium group still has one pair of electrons free; these are represented in the above formula by a dash.



nitrobenzene and an alkali benzene diazotate (p. 111). When boiled with alcohol it gives bromobenzene (p. 123).

**Phenyldiazonium nitrate**,  $[\text{C}_6\text{H}_5\cdot\text{N}_2]\text{NO}_3$ , forms long, colourless needles, which explode more violently than mercury fulminate or nitrogen iodide when gently heated, or when struck, or compressed.

**Phenyldiazonium sulphate**,  $[\text{C}_6\text{H}_5\text{N}_2]\text{HSO}_4$ , forms colourless prismatic needles, which explode at  $100^\circ$ . It is obtained either from the nitrate by the action of sulphuric acid, or from aniline sulphate by diazotisation (*Knoevenagel*, *Ber.* 28, 2049).

**Phenyldiazonium perchlorate**,  $[\text{C}_6\text{H}_5\text{N}_2]\text{ClO}_4$ , is, like potassium perchlorate, difficultly soluble in water. It separates in prismatic needles when perchloric acid is added to an aqueous solution of the diazonium chloride. It explodes violently even in the damp condition. (*Vörlander*, *Ber.* 39, 2713, 3146).

**Oxalate** (*Hantzsch*, *Ber.* 28, 2059). **Carbonate**, **nitrite**, **acetate**, see *Hantzsch*, *Ber.* 28, 1741.

The diazonium cyanides have been obtained in the form of their double salts with silver cyanide, e.g., *p*-bromophenyl-diazonium silver cyanide,  $\text{BrC}_6\text{H}_4\text{N}_2\cdot(\text{CN})\cdot\text{AgCN}$  (*Hantzsch*, *Ber.* 30, 2546; cf. also anisole-diazonium cyanide, *Euler*, *Ber.* 34, 4166). The diazonium cyanides isomerise very readily to diazocyanides (p. 121).

"**Diazobenzene thiocyanate**,"  $\text{C}_6\text{H}_5\text{N}_2\cdot\text{SCN}$ , is a yellow, very explosive substance obtained by the action of potassium thiocyanate on phenyl diazonium chloride. Apparently the compound is not really a diazonium salt, but belongs to the mixed azo-type. *p*-Chlorodiazobenzene thiocyanate,  $\text{ClC}_6\text{H}_4\text{N}_2\cdot\text{SCN}$ , readily isomerises to *p*-thiocyano-phenyldiazonium chloride  $(\text{CNS})\text{C}_6\text{H}_4\text{N}_2\text{Cl}$ . An exchange between nuclear substituted atoms and the anion of diazonium salts has been observed in a number of cases. It occurs only with substituents in the *o*- or *p*-positions. Thus, 2,4-dibromobenzene-diazonium chloride gives a chlorobromobenzenediazonium bromide, and 2,4,6-tribromobenzenediazonium chloride gives dibromochlorobenzenediazonium bromide (*Hirsch*, *Ber.* 31, 1253; *Hantzsch*, *Ber.* 33, 505; 36, 2069).

*p*-Phenylene-bisdiazonium chloride,  $\text{C}_6\text{H}_4(\text{N}_2\text{Cl})_2$ , forms yellow needles, and is very explosive (*Hantzsch*, *Ber.* 30, 92).

## 2. Diazohydrates and Diazotates. Isomerism

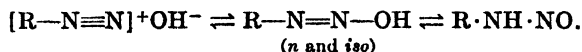
The diazotates and diazohydrates belong, according to their generally accepted constitution, to the type  $\text{R}-\text{N}=\text{N}-\text{Y}$ . With this arrangement of nitrogen atoms they would be classified as mixed azo-compounds (*Angeli*, however, regards them as mixed azoxy-compounds). The fact, however, that in the diazohydrates and diazotates the groups  $\text{Y} = \text{OH}$  and  $\text{O}^-$  are present, causes a displacement of the stage of oxidation and makes these compounds colourless. They are, further, closely related to the diazonium salts, so that they may justly be treated with the latter as "aromatic diazo-compounds." Compounds of the mixed azo-type in which  $\text{R} = \text{aryl}$ , and  $\text{Y} = \text{CN}$  (the so-called diazobenzene cyanides),  $\text{SO}_3\text{H}$  (so-called diazobenzene sulphonic acids), or  $\text{SO}_3\text{R}$ , are also usually regarded as belonging to this class. Although these substances show the intense colours of azo-compounds they are in equilibrium with the corresponding diazonium-salts,  $[\text{R}\cdot\text{NN}]^+\text{Y}^-$ . They will therefore be dealt with here. The yellow diazoamino-compounds ( $\text{Y} = \text{NHR}$ , where  $\text{R}$  is an aromatic radical) also readily split off a diazonium cation,  $[\text{X}\cdot\text{NN}]^+$ , and will also be considered. Those mixed azo-compounds, on the other hand, which are not reversibly connected with diazonium compounds, will be dealt with later with the azo-compounds.

When solutions of diazonium salts are made alkaline, the diazonium

cation and OH' ions can exist together in very dilute solution, as the absorption spectrum shows (*Hantzsch*, Ber. 45, 3031). At higher concentrations, however, the two combine, and the constitution of the diazo group changes, and a diazohydrate is formed:  $[R-N\equiv N]^+ + OH^- \rightarrow R-N=N-OH$ . This diazohydrate is not a base, but an acid, and reacts with a second hydroxyl ion with salt formation:  $R-N=N-OH + OH^- \rightarrow [R-N=N-O]^- + H_2O$ . The diazonium salt thus reacts with two equivalents of alkali to form an alkali-diazotate:  $[R-N\equiv N]^+Cl^- + 2KOH \rightarrow [R-N=N-O]^-K^+ + KCl + H_2O$ . This conversion of a diazonium salt into a diazotate is reversible. By the action of acids the diazotates, and the diazohydrates thus liberated, form diazonium salts.

The diazotates themselves exist in two forms: the "*n*-" and the "*iso*"-diazotates. The normal diazotates are the compounds formed first, but they change into the *iso*-diazotates to some extent at ordinary temperatures, or on heating (*Bamberger*, Ber. 29, 455). The latter differ from the *n*-diazotates in that they "couple" with aromatic amines or phenols to give azo-dyes, either not at all or with great difficulty (*Schraube* and *Schmidt*, Ber. 27, 514).

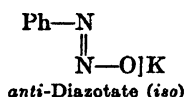
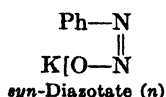
To explain this difference it was first assumed that the normal diazotates were derived from the type  $R-N=N-OH$ , whilst the *iso*-diazotates, which give phenyl-methyl-nitrosamines when treated with methyl iodide, were regarded as metallic salts of the primary nitrosamines,  $R-NH-NO$ , being desmotropic isomers of the *iso*-diazotates themselves. This explanation was proved to be false by *Hantzsch* (Ber. 35, 226, 2964; 45, 3036), who obtained in a number of cases, colourless, distinctly acidic primary products on treating *iso*-diazotates with acids. These products combine with dry ammonia to give ammonium *iso*-diazotates, and react with phenyl-isocyanate as hydroxyl compounds. After a time, especially when dissolved in indifferent solvents like benzene, they rearrange into yellow, less acidic nitrosamines. In other solvents, *e.g.*, in ether, these nitrosamines are partly reconverted into *iso*-diazo hydrates, and they are reconverted into *iso*-diazotates by caustic alkalis. The primary nitrosamines are thus special desmotropic forms of the hydrogen compounds, and are not the acids of the *iso*-diazotates. This makes altogether four different isomeric forms: diazonium hydroxide, existing only in very dilute solution in the form of ions, the normal and *iso*-diazo-hydrates, and nitrosamine. They are all interconvertible:



It is to be observed that the free *n*-diazohydrates are unknown, since they either anhydridise or rearrange at once into other isomers. In water the dominant equilibrium is that between diazonium ions and hydroxyl ions on the one side and diazohydrate and its anions on the other. The equilibrium varies with concentration, the pH of the solution, and the substituents in the aromatic nucleus.

According to *Hantzsch*, the isomerism of the diazotates is not to be regarded as structural isomerism, but as *stereoisomerism*, and more

particularly as *cis-trans isomerism* about the N=N double bond (*cf.* Vol. I, p. 36 and this vol., p. 273, benzaldoxime) as shown by the formulae:



The difference in ease of coupling and other differences between the normal and *iso*-diazotates is explained by *Hantzsch* as due to the greater energy content of the normal, or *syn*-diazotates. The two forms could also be called *labile* (*n* or *syn*) and *stable* (*iso* or *anti*) diazotates (*cf.* dynamic isomerism, Vol. I, p. 34).

*Angeli* (Ber. 59, 1400; 62, 1924, 2101; 63, 1977), on the other hand, regards the normal and *iso*-diazotates as structurally isomeric, like the *as*-azoxy-compounds (p. 134), the *n*-diazotates having the oxygen attached to the  $\beta$ -nitrogen, and the *iso*-diazotates to the  $\beta$ -nitrogen. The (hypothetical) normal hydrate would then be R—N(O)=NH, and the isohydrate R—N=(O)NH. In terms of the octet theory the oxygen atoms in the above formulae would be said to be linked by semipolar bonds, as in the amino oxides, azoxy-compounds, *etc.*, and the formula of the isodiazohydrate would differ from the customary hydroxyl formula only by the position of the proton, a difference which disappears when salt formation takes place. Hence there is no constitutional difference between the formulae of *Hantzsch* and *Angeli* as regards *iso*-diazotates, though there is a difference with that of the *n*-diazotates. *Cambi* and *Szegoe* (Ber. 61, 2087) have found a band in the ultra-violet absorption spectrum of the *iso*-diazotates which does not appear in that of the *n*-diazotates, and conclude that the isomerism cannot be merely spatial. For *Hantzsch's* counter-arguments see Ber. 66, 667; 62, 1235; 63, 1270; 64, 655. *Hantzsch's* view is supported by the fact, not easily reconciled with the view of *Angeli*, that the normal diazotates are the first to be formed from diazonium salts, and that they couple more easily to form azo-dyes, and also that a similar type of isomerism occurs with labile and stable forms of diazo cyanides and other compounds which are undoubtedly of the mixed azo type, R—N=N—X. An argument in favour of *Angeli's* view, on the other hand, can be found in the formation of *iso*-diazotates from the primary nitrosamines, in which the double bond between the nitrogen atoms is not present, whereas *n*-diazotates are not directly produced from these compounds.

(a) **NORMAL (*syn*- or LABILE) DIAZOHYDRATES.** These compounds are not known in the free state. When attempts are made to liberate them from their potassium salts by the addition of acids, under certain conditions, extremely unstable, explosive yellow precipitates are obtained, which appear to be anhydrides, and not hydrates, *e.g.*, diazobenzene anhydride,  $[\text{C}_6\text{H}_4\text{N}_2]_2\text{O}$ , and *p*-chlorodiazobenzene anhydride,  $[\text{ClC}_6\text{H}_4\text{N}_2]_2\text{O}$ . These substances dissolve in acids to form diazonium salts, and in alkalis to form diazotates. They give *bis*-diazooamino compounds with ammonia, diazoamino compounds with aniline, diazo-cyanides with hydrocyanic acid, and diazo-sulphones with benzene-sulphinic acid (*Bamberger*, Ber. 29, 451; *Hantzsch*, *ibid.* 31, 637). Phenyl-diimide has been observed as an unstable intermediate product in the reduction of the normal diazo-hydrate (*Angeli*, Ber. 62, 2009).



***n*-Potassium phenyldiazotate**,  $C_6H_5N_2OK$ , is formed when a saturated aqueous solution of phenyldiazonium chloride is slowly added to an excess of a concentrated solution of caustic potash (Bamberger, Ber. 29, 461). It forms soft nacreous flakes, which can be reconverted into phenyldiazonium chloride. The corresponding sodium salt is obtained in small quantities when sodamide acts upon nitrosobenzene (Bamberger, Ber. 37, 629), or when hydroxylamine acts upon nitrosobenzene in alkaline solution (Hantzsch, Ber. 38, 2056). Potassium phenyldiazotate reacts with alcohols even in the cold giving diazo-esters (Bamberger, Ber. 29, 448). On reduction phenylhydrazine is obtained (Hantzsch, Ber. 30, 339). Oxidation of alkaline solutions of benzene diazonium compounds with potassium ferricyanide, potassium permanganate or hydrogen peroxide gives mainly phenyldiazotic acid, in addition to small amounts of nitrosobenzene (p. 67), nitrobenzene (p. 60), azobenzene (p. 137), nitroso-phenyl-hydroxylamine (p. 70) and diphenyl. *n*-Potassium phenyldiazotate is converted by benzoyl chloride and sodium hydroxide into nitrosobenzanilide,  $C_6H_5N(NO) \cdot COC_6H_5$  (Bamberger, Ber. 30, 214; Hantzsch, Ber. 32, 1718). Salts of the heavy metals have been obtained by precipitating a solution of the potassium salt with salts of the metals (Curtius, Ber. 23, 3035; Bamberger, Ber. 28, 226).

**Diazobenzene methyl ether**,  $C_6H_5N_2OCH_3$ , isomeric with methyl-phenyl-nitrosamine (p. 111) is obtained by the action of methyl iodide on *n*-, or better, *iso*-silver phenyldiazotate, by the action of methyl alcohol on potassium phenyldiazotate, or by reducing the methyl ether of nitroso-phenyl-hydroxylamine (Staudinger, Ber. 49, 1961, 1969). It is a yellow oil, volatile, and possessing a penetrating, stupefying odour; it darkens rapidly on exposure to air, and decomposes spontaneously soon after having been prepared. *o*- and *p*-Nitrodiazobenzene methyl ethers,  $NO_2C_6H_4N_2OCH_3$ , see Bamberger, Ber. 28, 227, 236. When acted upon by alkali in the cold the diazo ethers give normal diazotates (Hantzsch, Ber. 36, 4361).

**Di-*p*-nitrophenyldiazo-sulphide**,  $(NO_2C_6H_4N_2)_2S$ , is an egg-yellow, very explosive substance obtained by adding  $H_2S$  to a neutral solution of the diazonium chloride. With benzene it gives *p*-nitrodiphenyl, nitrogen, and sulphur, together with some di-*p*-nitrophenyl disulphide. When an acid solution of 4-nitrophenyldiazonium chloride is treated with excess of  $H_2S$ , *p*-nitrophenyldiazomercaptan hydrosulphide,  $NO_2C_6H_4N_2SH \cdot H_2S$ , is formed in red needles with a metallic lustre, which dissolve in alkalis with a deep red colour. Dinitrophenyldiazo-sulphide is formed at the same time as the above hydrosulphide, which decomposes on melting giving nitrophenylhydrazine, nitraniline, sulphur, and dinitrophenyl disulphide. A third product of the action of  $H_2S$  is di-*p*-nitrophenyldiazo disulphide,  $[NO_2C_6H_4N_2]_2S_2$ , which is formed as sulphur-yellow needles, soluble in acetone. It is not explosive, and is insoluble in alkalis (Bamberger, Ber. 29, 272).

(b) **ISO-(anti- or STABLE) DIAZOHYDRATES** are liberated from their potassium salts by acetic acid. They are very unstable substances. Those derived from benzene and toluene are colourless oils. They are not really hydrates, but neutral *pseudo*-forms, the primary aryl-nitrosamines,  $ArNH \cdot NO$ . In a few cases, however, as, for example, with dibromoanisole diazohydrate, the hydroxyl forms have been isolated as unstable precipitates which readily change to nitrosamines. In non-dissociating solvents these hydrates react readily with  $NH_3$ , acetyl chloride, and  $PCl_5$ , whilst the nitrosamine forms are relatively unaffected by these reagents (Hantzsch, Ber. 35, 2964; 45, 3036).

**Potassium phenylisodiazotate**,  $C_6H_5N_2OK$ , is formed when the normal potassium compound is heated for a short time with concentrated  $KOH$  to 130–135° (Schraube, Ber. 27, 514). It is also formed by fusing phenyl-methyl-nitrosamine with potash (p. 111). It is reconverted into the nitrosamine by treatment with methyl iodide (Schraube, Ber. 27, 514; Pechmann, Ber. 27, 672; Bamberger, Ber. 27, 680). It is reduced smoothly by sodium amalgam to phenylhydrazine (Bamberger, Ber. 29, 473; Hantzsch, Ber. 30, 339). It reacts like a normal diazotate towards benzoyl chloride and caustic soda, and oxidising agents (*cf.*, however, p. 122); but, unlike the latter, it fails to give dyes with phenols, *e.g.*,  $\beta$ -naphthol, in alkaline solution (Schraube, Ber. 27, 517). Potassium phenylisodiazotate is also formed directly from aniline and phenylhydrazine by the action of an alkyl nitrite or alkali alcoholate; in the latter case nitrous oxide is given off (Bamberger, Ber. 33, 3511; Thiele, Ber. 41, 2808). It has also been obtained from

hydroxyazoxybenzene,  $C_6H_5(N_2O)C_6H_4(OH)$ , by oxidation with permanganate. Potassium toluene-*p*-isodiazotate is formed from its normal isomeride simply on exposure to air. Sodium *p*-nitrobenzene isodiazotate,  $(NO_2)C_6H_4N_2ONa + 2H_2O$ , gives nitrophenyl-methyl-nitrosamine with methyl iodide, whereas the silver salt gives the isomeric diazo-ester. Bleaching powder oxidises it to *p*-nitrophenyl-nitramine (Zincke, Ann. 330, 36).

(c) DIAZOBENZENE SULPHONIC ACID, benzene azosulphonic acid,  $C_6H_5N_2SO_3H$ , is very unstable (Hantzsch, Ber. 30, 75). Its potassium salt is formed when phenyl diazonium nitrate is added to a neutral or weakly alkaline, cold solution of potassium sulphite. The liquid solidifies to a yellow crystalline mass. Under other conditions a more readily decomposed orange salt is formed (Hantzsch, Ber. 27, 1715; Bamberger, Ber. 27, 2930). Phenyl diazonium sulphonates are photosensitive, and have been used in photography (Green, Ber. 23, 3131). Diazobenzene nitrate is reduced by potassium bisulphite to phenylhydrazine sulphonate (p. 146) and this gives potassium diazobenzene sulphonate on oxidation with  $HgO$  (Paal, Ber. 27, 1245).

Potassium *p*-nitrophenyl diazonium sulphonate, is obtained from *p*-nitrophenyl diazonium nitrate by the action of an equivalent quantity of  $K_2SO_3$ ; it appears to exist in two forms. The acid crystallises in ruby-red prisms with  $4H_2O$  (Hantzsch, Ber. 30, 90). With two mols.  $K_2SO_3$ , on the other hand, potassium *p*-nitrophenylhydrazine disulphonate,  $C_6H_4(NO_2)N(SO_3K)NH \cdot SO_3K$  (p. 147) is formed (Bamberger, Ber. 29, 1829). *p*-Chloro- and *p*-bromo-phenyl diazonium sulphonic acids have also been prepared (Hantzsch, Ber. 30, 75).

Diazonium salts combine with benzene sulphinic acid a transformation occurring and benzene diazosulphones are formed. They are decomposed by  $HCl$  and diazonium chlorides and sulphinic acids are re-produced (Hantzsch, Ber. 30, 312; Bamberger, Ber. 32, 638). On the other hand benzene sulphinic acid combines with substances containing the grouping  $C_6H_5N:NX$  such as phenyl diazonium cyanide, the azo-compounds (p. 135), etc., to form colourless addition products, of the type  $C_6H_5N(SO_2C_6H_5)NHX$ , which are in most cases unaffected by water and acids. They should be regarded as derivatives of hydrazobenzene. They are decomposed by alkalis, their components being reformed. True diazonium sulphinates of nitro-groups are introduced into the components: *o*-nitrophenyl diazonium-*o*-nitrobenzene sulphonate,  $[NO_2C_6H_4N_2][SO_2C_6H_4NO_2]$ , is a yellow precipitate, which usually explodes at  $100^\circ$ , obtained from *o*-nitrophenyl diazonium solutions and sodium *o*-nitrobenzene sulphonate (Clausz, Ber. 44, 1415). The action of  $SO_2$  on *p*-nitrophenyl diazonium hydroxide gives *p*-nitrophenyl-diazo-*p*-nitrophenyl-sulphone,  $NO_2C_6H_4N:NSO_2C_6H_4NO_2$  (Ekson, Ber. 35, 661).

PHENYLDIAZONIUM CYANIDE, phenyl-azo-carboxylic nitrile,  $C_6H_5N:NCN$  is an unstable oil formed by adding potassium cyanide to the solution of a phenyl diazonium salt. If the process is carried out in the reverse order, the diazonium salt being added to the potassium cyanide, an addition product of hydrocyanic acid is formed,  $C_6H_5N_2CN \cdot HCN$ ; it separates as a yellow oil, m.p.  $70^\circ$  (cf. p. 161). Hydrogen peroxide converts it into whitish-yellow needles of phenyl-azoxy-carboxylic amide,  $C_6H_5 \cdot N(O)NCONH_2$ , m.p.  $151^\circ$  (decomp.) (Angeli, Atti. Accad. Lincei, 26, I, 95, 207). Phenyl-azo-carboxylic amide, p. 138.

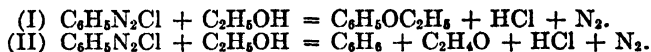
A number of substituted phenyl diazonium cyanides have been obtained in two distinct forms, one unstable and the other stable, *syn*- and *anti*-forms (p. 119). The unstable, low-melting modifications are formed only at low temperature. They lose nitrogen very readily, especially in the presence of copper powder, forming phenyl cyanides; they couple (p. 118) and change rapidly into the stable isomers, especially in alcoholic solution and in sunlight (Ciusa, Atti. Accad. Lincei 15, II, 136). This rearrangement is affected by the nature and position of the nuclear substituents. Labile *p*-chloro- and *p*-nitrodiazobenzene cyanides melt at  $28^\circ$  and  $29^\circ$ , respectively, and the stable modifications at  $106^\circ$  and  $86^\circ$ , respectively. 2,4,6-Tribromophenyl diazonium cyanide, labile form m.p.  $60^\circ$ , stable form, m.p.  $147^\circ$ . The intensely coloured unstable diazonium cyanides change in aqueous solution into weakly coloured or colourless diazonium cyanides, or, more accurately, into the ions of the latter:  $R \cdot N \equiv N - CN \rightleftharpoons [RN_2]^+ + CN^-$ . The stable diazonium cyanides do not behave in this way, but react like ordinary azo-compounds (p. 135). Most of them combine readily with hydrocyanic acid to give imido-cyanides, with water to form azo-carboxylic amides, and with alcohols to form imido ethers, from which the potassium salts of the

corresponding phenyl-azo-carboxylic acids can be obtained by the action of potash. The acids themselves are very unstable. Tribromophenyl-azo-carboxylic acid,  $C_6H_2Br_3 \cdot N_2COOH$  has been obtained from its amide, which is an oxidation product of tribromophenyl-semicarbazide (*Hantzsch*, Ber. 28, 670, 2073; 30, 2529, 2553; *Widman*, Ber. 28, 1925).

### *The More Important Decomposition Reactions of the Diazonium Salts*

In the decomposition of diazonium salts nitrogen is evolved and other atoms or groups occupy its place. These reactions shed much light on the mutual relationships between many di- and poly-substitution products of benzene and its homologues (see p. 8). For the corresponding reactions of aliphatic diazo-compounds see Vol. I, p. 459.

1. *Replacement of the diazo-group by hydrogen.*—(a) When diazonium salts are heated with alcohols, two reactions may occur:



In (I) phenol ethers are produced, and in (II) benzene hydrocarbons with aldehydes as by-products (*Griess*, Ann. 137, 69; *Fischer*, Ber. 9, 899; *Remsen*, Ber. 18, 65). Often both reactions go on simultaneously. Solid phenyl diazonium chloride or sulphate gives anisole with dry methyl alcohol, and phenetole, together with a little benzene, with ethyl alcohol, while the reaction which predominates with the acylated benzenes is the replacement of the diazonium group by hydrogen. Polyhydric alcohols seem to give phenolic ethers exclusively (*Hantzsch*, Ber. 34, 3337; 35, 998; 36, 2061). In sunlight, reaction (I) predominates (*Orton*, Proc. 21, 168).

When the diazonium salts are heated with phenols, nitrogen is evolved and phenol ethers are formed to some extent, though hydroxy-diphenyls are the main products of the reaction (*Norris*, Am. Chem. J. 29, 120).

(b) On reduction the diazonium compounds give aryl-hydrazines, e.g., phenylhydrazine. When these are boiled with oxidising agents such as  $CuSO_4$ ,  $FeCl_3$ ,  $K_2CrO_4$ , or  $NaOCl$ , nitrogen is evolved and a hydrogen atom takes the place of the hydrazine group:



The following reactions, in which hydrogen replaces the diazonium group, are probably due to the intermediate formation of aryl diimines,  $Ar \cdot NH:NH$ , and their spontaneous decomposition into nitrogen and the aromatic hydrocarbon (*Goldschmidt*, Ber. 46, 1529):

(c) boiling diazonium chlorides with stannous chloride solution (*Culmann*, Ber. 22, R 741);

(d) action of hypophosphorous acid on diazonium salts (*Mai*, Ber. 35, 162; *Vorländer*, Ann. 320, 143);

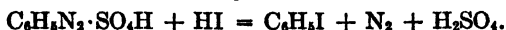
(e) dissolving the diazonium compound in caustic soda and adding sodium stannite (*Eibner*, Ber. 36, 813), often with simultaneous formation of diphenyl compounds; *iso*-diazotates are not reduced by alkaline stannite (*Hantzsch*, Ber. 36, 2065).

(f) Boiling formic acid converts the diazonium salts almost exclusively into the corresponding hydrocarbons:



The sole products of the action of glacial acetic acid are acetyl-phenols (*Orton*, *J.* 91, 35; *Tobias*, *Ber.* 23, 1632).

2. *Replacement of the diazonium group by halogen.*—(a) The diazonium salts are treated with hydrogen halides. Of the four, hydriodic acid reacts most readily:



The hydrogen halides are often used in glacial acetic acid solution.

A modification of the method consists in treating amine hydrobromides or hydriodides with nitric acid.

(b) The action of concentrated halogen hydracids on diazo-amino compounds. This reaction was applied by *Wallach* (*Ann.* 243, 219) to the preparation of fluoro- and chloro-derivatives:



(c) Chloro- and bromo-compounds are also obtained when the double salts of diazonium chlorides or bromides with  $\text{PtCl}_4$  or  $\text{PtBr}_4$  are heated alone, or better, when mixed with sodium carbonate or chloride:



Still better, the double salts with  $\text{HgCl}_2$  and  $\text{HgBr}_2$  may be used (*Schwechter*, *Ber.* 65, 1605).

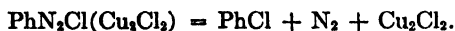
(d) Bromo-compounds may be prepared by boiling diazonium perbromides with ethyl alcohol, which is oxidised to aldehyde, bromobenzenes being formed:



(e) To replace the diazonium group by fluorine, the best method is to use the diazonium borofluorides, e.g.,  $[\text{PhN}_2]^+[\text{BF}_4]^-$  (*Balz*, *Ber.* 60, 1186).

The reactions (a)–(d) were discovered by *Griess*. *Sandmeyer* discovered a reaction, based on the decomposition of diazonium salts by cuprous compounds, which is of wide application (*Ber.* 17, 2650; 23, 1880).

(f) If an aqueous solution of phenyldiazonium chloride is treated with cuprous chloride an addition compound,  $\text{PhN}_2\text{Cl}\cdot\text{Cu}_2\text{Cl}_2$  is first formed, which decomposes to  $\text{PhCl}$  on warming (*Lellmann*, *Ber.* 19, 810; *Erdmann*, *Ann.* 272, 141; *Hantzsch*, *Ber.* 33, 2544; *Heller*, *Ber.* 44, 250; *Wantig*, *Ber.* 46, 3923):



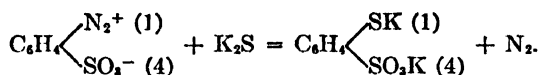
Cuprous bromide and iodide react with the corresponding diazonium salts in a similar way. If cuprous bromide is allowed to act on a diazonium chloride, the corresponding bromobenzene is the chief product under suitable conditions. This proves that the cuprous halide plays an essential part in the reaction.

A modification of this process was discovered by *Gattermann* (*Ber.* 23, 1218; 25, 1091). The diazo-compound is treated with copper powder in the presence of  $\text{HCl}$ ,  $\text{HBr}$ , or  $\text{HI}$ . The action of the copper seems to be mainly catalytic.

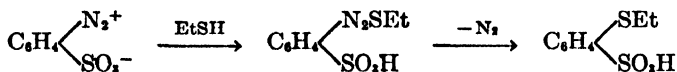
3. *Replacement of the diazo-group by hydroxyl.*—When diazonium salts (preferably sulphates) are boiled with water or a solution of copper sulphate, the diazo-group is replaced by hydroxyl, as men-

tioned on p. 112. This method often fails with negatively substituted diazonium salts but will take place in these cases too, if the water is replaced by a mixture of dilute sulphuric acid and sodium sulphate (*Cain*, Proc. 21, 206). When nitrates are used nitro-phenols are obtained as by-products. The velocity of this reaction has been measured by *Euler* (Ann. 325, 292).

4. *Replacement of the diazo-group by the —HS group.*—When phenyl-diazonium-*p*-sulphonic acid (p. 178), the product of diazotising sulphanilic acid, is heated with an alcoholic solution of potassium sulphide, the potassium salt of *p*-thiophenol-sulphonic acid is formed (*Klason*, Ber. 20, 350):



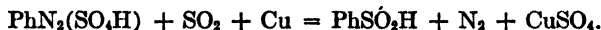
Mercaptan combines with diazotised sulphanilic acid forming a compound which breaks up at higher temperatures, into nitrogen and thiophenol-ethyl ether *p*-sulphonic acid:



With xanthates (Vol. I, p. 489) the diazonium salts form xanthic esters, such as  $\text{PhS} \cdot \text{CSOEt}$ , which give thiophenols on hydrolysis (*Leuckari*, J. pr. 41, 184).

The diazonium salts react with thioglycollic acid (Vol. I, p. 429) with formation of difficultly soluble glycollates, such as  $\text{PhN}_2 \cdot \text{S} \cdot \text{CH}_2\text{COOH}$ , which are converted into *aryl-thioglycollic acids*, e.g.,  $\text{PhS} \cdot \text{CH}_2\text{COOH}$ , on warming, nitrogen being evolved (Ger. Pat. 194,040). The formation of di-*p*-nitrophenyl disulphide by decomposition of the corresponding diazo-sulphide and diazo-mercaptan has been mentioned above (p. 120).

5. *Replacement of the diazo-group by the sulphinic radical* is effected by passing sulphur dioxide into a solution of a diazonium sulphate, or by treating the latter with an alcoholic solution of  $\text{SO}_2$  and bisulphite, and subsequently decomposing the product with Cu powder (*Gattermann*, Ber. 32, 1136; Ger. Pat. 130,119).



6. *Replacement of the diazo-group by the nitro-group.*—If freshly precipitated cuprous oxide is added to a solution of a diazonium nitrite, or if copper powder is added to a solution of the double compound of a diazonium nitrate and mercuric nitrite, e.g.,  $\text{PhN}_2\text{NO}_3 \cdot \text{Hg}(\text{NO}_2)_2$ , the diazo-group is replaced by the nitro-group (*Hantzsch*, Ber. 33, 2551).

7. In some cases the diazo-group can be replaced by an amine residue, thus *Wagner* (Ber. 35, 2593) has succeeded in replacing the diazo-group of the diazonium betaine of aminoanthraquinone sulphonic acid by an amine radical by the action of ammonium carbonate or amines.

8. *Replacement of the diazo-group by the CN group.*—The importance of this reaction has already been pointed out (p. 13). It connects the nitro-amino benzenes with the nitrobenzoic acids, and these with the phthalic acids. The diazonium chloride solution is added to a solution of copper sulphate mixed with potassium cyanide (p. 121):

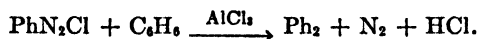


(*Sandmeyer*, Ber. 20, 1495; *Tobias*, Ber. 23, 1630).

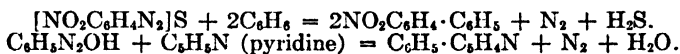
9. Potassium thiocyanate and cuprous thiocyanate act in a similar way on diazonium salts, the diazo-group being replaced by the thiocyanate group (p. 117) (*Thurnauer*, Ber. 23, 770).

10. When potassium cyanate and powdered copper are added to a solution of a diazonium sulphate, phenyl isocyanate or carbanil (p. 97) is obtained (*Gattermann*, Ber. 25, 1086).

11. *Formation of diphenyl compounds from diazo-compounds.*—Diphenyl compounds are often obtained as by-products when diazo-compounds are treated with reducing agents, such as  $\text{SnCl}_2$  (*Grüss*, Ber. 18, 965), EtOH and Cu (*Gattermann*, Ber. 23, 1226), EtOH alone, EtONa (*Oddo*, Ber. 28, R 389), and also in reactions with water, phenol (*Hirsch*, Ber. 23, 3405) (p. 122), and potassium ferricyanide (*Bamberger*, Ber. 26, 471). Using anhydrous formic acid or EtOH as reducing agents, and then decomposing with copper powder, *Gerngross* and *Jonas* (Ber. 57, 747) isolated diphenyl, terphenyl (= *p,p'*-diphenylbenzene), quaterphenyl (= *p,p'*-diphenyl-diphenyl), and quinquephenyl (= *p*-diphenyl-*p'*-diphenylbenzene). The phenyl group can be introduced into many aromatic hydrocarbons and heterocyclic compounds, such as thiophene, pyridine, and quinoline, by means of a diazonium chloride, preferably in the presence of  $\text{AlCl}_3$  (*Möhlau*, Ber. 26, 1994).



The diazo-residue in diazo-oxides, -sulphides, and *iso*-diazo-hydrates (p. 120) is also readily replaced by cyclic radicals (*Bamberger*, Ber. 28, 404; 29, 274, 452; *Kühling*, Ber. 29, 165).



12. On treatment with ammoniacal cuprous oxide most diazonium salts lose nitrogen and are converted into azobenzenes:



The diazonium salts obtained from *o*- and *p*-nitraniline, and from anthranilic acid, however, give the corresponding diphenyl derivatives (*Vorländer*, Ann. 320, 122).

13. When diazonium salts are treated with a saturated solution of potassium ferricyanide, reactions 11 and 12 take place simultaneously and compounds of the diphenyl series are formed; thus, with benzene diazonium chloride, benzene-azo-diphenyl,  $\text{PhN:NC}_6\text{H}_4\cdot\text{Ph}$ , is formed (*Ehrenpreis*, C. 1907, I, 1789).

*Other reactions of the diazo-compounds*, in which no nitrogen is eliminated.

1. Diazonium salts are reduced to phenyl-hydrazines (p. 146).

Ethyl phenyl-hydrazines and diethyl-benzidine are formed when phenyl diazonium chloride acts upon  $\text{ZnEt}_2$  in ether solution (*Bamberger*, Ber. 35, 1479; *Tichwinski*, J. Russ. Phys. Chem. Soc. 36, 1052).

2. Diazonium compounds are oxidised to nitroso-benzene (p. 67) and phenyl-nitramine (p. 111) in alkaline solution.

3. The behaviour of diazonium compounds towards ammonia, alkyl-anilines, aniline and related bases and phenols, when diazo-imino- (p. 131), diazo-amino- (p. 126), and amino-azo- (p. 138) or hydroxy-azo-compounds are formed should be particularly noted. These very important reactions will be discussed in detail in connection with the individual classes of compounds.

4. When diazonium salts act upon compounds with the  $\text{CH}_3\text{CO}$  grouping, hydrazones or mixed azo-compounds (p. 138) are formed.

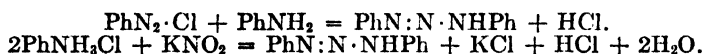
The hydrazones may react with a further quantity of the diazonium salt forming *formazyl* compounds, of the amidine type (*Bamberger*, Ber. 27, 147; 29, 1386; *Pechmann*, Ber. 27, 320, 1679; *Bülow*, Ber. 31, 3122, 32, 2880).

5. Some diazo-compounds, particularly nitro- and polyhalogen diazonium salts, couple directly with butadiene, isoprene, and similar doubly unsaturated aliphatic hydrocarbons, forming mixed azo-compounds (*Meyer*, Ber. 52, 1468).

### (i) Diazoamino- and (k) bis-Diazoamino-compounds

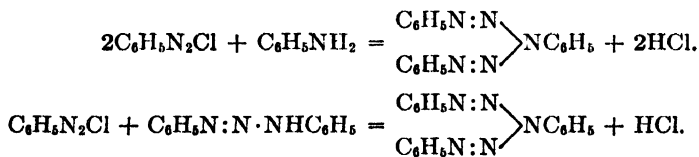
The *diazoamino-compounds* are derived from the unknown hydride *triazene*,  $\text{NH}=\text{N}-\text{NH}_2$ , the *amidine of nitrous acid* (*Thiele*, Ann. 305, 65). The hydrogen of the imino-group is replaced by aromatic radicals such as phenyl, tolyl, etc., while the hydrogen of the amino-group may be replaced by either aliphatic or aromatic residues, when *mixed* or *true aromatic diazoamino compounds* are formed. The *bis-diazoamino compounds* are derived from the nitrogen hydride,  $\text{NH}=\text{N}-\text{NH}-\text{N}=\text{NH}$ , also unknown.

*Methods of formation of diazoamino-compounds.*—These compounds are produced by the action of primary or secondary amines on diazonium salts. (1a) Primary amines give diazoamino- or *bis*-diazoamino-compounds, according to the conditions. Diazoamino-compounds are formed by the interaction of equimolecular amounts of a diazonium salt and a primary amine, and also by the action of an alkali metal nitrite on a salt of a primary amine in the absence of mineral acids:



Substituted anilines containing the substituent in the *p*- or *o*-position react, in the main, like aniline itself, but meta-derivatives, such as *m*-toluidine, give chiefly aminoazo-compounds (p. 138) (*J.* pr. 65, 401).

(1b) A *bis*-diazo compound is formed if one molecule of aniline is allowed to react in alkaline alcoholic solution with two molecules of a diazonium salt. The same compound is also obtained by the action of a diazonium chloride on diazoamino-benzene (*Pechmann*, Ber. 27, 703):



Primary aliphatic amines react very readily with a diazonium chloride, forming *bis*-diazoamino compounds, so that the isolation of simple aliphatic-aromatic diazoamino compounds is only practicable under special conditions (*Dimroth*, Ber. 38, 2328).

When a phenyl diazonium salt solution is allowed to flow into cold, concentrated ammonia, *bis-diazobenzene-amide*,  $\text{PhN:N}\cdot\text{NH}\cdot\text{N:NPh}$ , is the only product (*Pechmann*, Ber. 28, 171).

Normal alkali diazotates also furnish diazoamino-compounds. The reaction is discussed in detail by *Schraube*, (*Ber.* 29, 289). The *iso*-diazotates, obtained by isomerisation of the *n*-compounds, do not usually react.

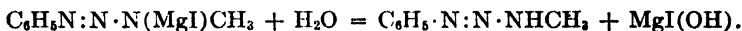
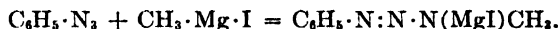
(1c) Secondary aromatic and aliphatic bases yield secondary aromatic or mixed aliphatic-aromatic diazoamino-compounds (*Baeyer*, *Ber.* 8, 148; *Vignon*, *C.r.* 140, 1038).

(2) Diazoamino-compounds are also obtained by the action of nitrous acid on alcoholic solutions of primary amines, the free diazo-benzene hydroxide or anhydride first formed reacting with a further quantity of aniline (p. 119).



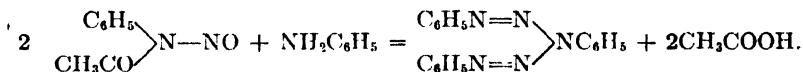
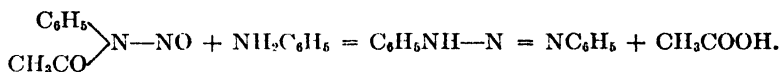
If nitrites, *e.g.*,  $\text{AgNO}_2$ , act upon free aniline, salts of diazoamino-compounds, *e.g.*,  $\text{PhN}_2\cdot\text{NAgPh}$  are formed (*Niementowski*, *Ber.* 29, R 1158).

(3) A convenient method for the preparation of mixed aliphatic-aromatic diazoamino-compounds consists in the action of organo Mg-compounds on the aryl azides. Addition products are first formed from which the diazoamino-compounds are liberated by water (*Dimroth*, *Ber.* 38, 683):

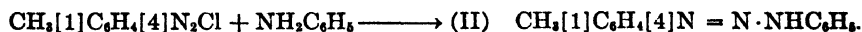
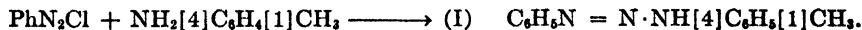


(4) Diazoamino-compounds are also produced by the interaction of nitrosamines and primary amines, *e.g.*, diazoaminotoluene from diphenyl-nitrosamine and *p*-toluidine, the nitroso-group acting like nitrous acid (*Pechmann*, *Ber.* 27, 655).

Nitroso-acetanilide (p. 111) reacts with aniline to give acetic acid and diazoaminobenzene. If two mols. of nitroso-acetanilide are used to one of aniline in alkaline solution, an aromatic *bis*-diazoamino compound is obtained:



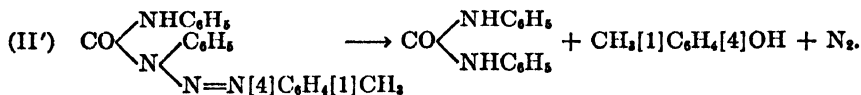
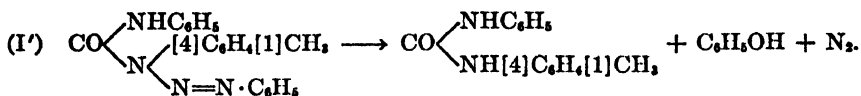
*Mechanism of the formation of diazoamino-compounds.*—It is a remarkable fact that in a reaction such as that between phenyl diazonium chloride and *p*-toluidine the same phenyl diazo-*p*-aminotoluene is formed as that which is obtained from *p*-tolyl-diazonium chloride and aniline, although two different compounds would be expected.



By method (3) identical products are obtained from phenyl azide and *p*-tolyl-magnesium bromide and from *p*-tolyl azide and phenyl magnesium bromide.

The constitution of the resulting substances is best determined by means of phenyl isocyanate, which converts them into substituted ureas. The urea formed with diazobenzene-*p*-aminotoluene, for example, must have the structure (I') or (II'), according as whether formula (I) or (II) is the correct one for the diazo-amino-compound:

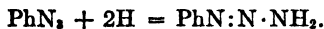




The decomposition products of this substituted urea when it is treated with dilute sulphuric acid, are *p*-phenyl-*p*-tolyl urea, phenol, and nitrogen, which agrees with formula (I'). Formula (II') would require the formation of *sym*-diphenylurea, *p*-cresol, and nitrogen. Hence diazobenzene-amino-*p*-toluene has the structure (I).

The imido-group seems to be attracted to the more negative radical, *e.g.*, to a radical containing Br or NO<sub>2</sub>. *Dimroth* (Ber. 40, 2395) has suggested an explanation for this rather surprising fact.

**DIAZOAMINO-COMPOUNDS FROM PRIMARY AROMATIC BASES.** Diazobenzene-amide, phenyltriazene, PhN:N·NH<sub>2</sub>, m.p. 50° (decomp.) is the simplest possible aromatic diazo-amino-compound. It cannot be prepared by the action of ammonia on phenyl-diazonium chloride, by which reaction only *bis*-diazobenzene-amide is formed. It has been obtained by the reduction of phenyl azide with SnCl<sub>2</sub> and HCl in ether at -18° (see the reduction of aliphatic diazo-compounds, Vol. I, p. 460).



The *cuprous salt* forms yellow, prismatic crystals. Diazobenzene-amide is very unstable, decomposing rapidly on standing and instantly in contact with acids, into aniline and nitrogen. It combines with phenyl isocyanate forming *benzene-diazo-phenylurea*, PhN:N·NHCO·NHPh. Oxidising agents, such as potassium hypobromite, or ammoniacal silver nitrate convert it into phenyl azide (*Dimroth*, Ber. 40, 2376).

**Diazoamino-benzene**, PhN=N=NPh, explodes when rapidly heated. It is formed by adding nitrous acid to a cold alcoholic solution of aniline (*Griess*, Ann. 121, 258), by mixing phenyl-diazonium nitrate and aniline (*Griess*, Ber. 7, 1619), or by mixing aniline hydrochloride, or aniline sulphate (*V. Meyer*, Ber. 8, 1074) with a cold solution of sodium nitrite (*B. Fischer*, Ber. 17, 641; 20, 1581; *Staedel*, Ber. 19, 1953). Phenyl azide (p. 132) and phenyl magnesium bromide combine to form a salt, PhN<sub>2</sub>N(MgBr)Ph, which is derived from diazoaminobenzene, and into which it is converted by water (*Dimroth*, Ber. 36, 910). Diazoaminobenzene crystallises in lustrous golden flakes or prisms; when quite pure, however, it is only very pale yellow in colour, and melts at 99° (*Rosenhauer*, Ber. 61, 396). It is insoluble in water, sparingly soluble in hot alcohol, ether, and benzene. Its reactions will be discussed later. The most important of them is its rearrangement into the isomeric *amino-azobenzene* (p. 129).

Its salts are very unstable, but a double salt (C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>·HCl)<sub>2</sub>PtCl<sub>4</sub>, crystallising in reddish needles, is obtained with HCl and PtCl<sub>4</sub>. For the hydrochlorides, see *Yokojima*, J. Soc. Chem. Ind. Japan, 1928. Cold acetic acid converts it into *benzene-diazoamino-azobenzene*, m.p. 119.5° (see below), which is presumably

an intermediate product in the rearrangement to amino-azobenzene. When an alcoholic solution of diazoamino-benzene is mixed with a solution of silver nitrate, red needles of a compound  $\text{PhN}_2 \cdot \text{N} \cdot \text{Ag} \cdot \text{Ph}$  separate. With sodium in ether it gives  $\text{PhN}_2 \cdot \text{N} \cdot \text{Na} \cdot \text{Ph}$ , which is decomposed by water (*Bekk*, Ber. 27, 2315). Cuprous salt, see *Meunier*, Bull. [3] 23, 103. Benzene-diazo-acetanilide,  $\text{PhN:N} \cdot \text{N}(\text{COMe})\text{Ph}$ , m.p.  $130^\circ$  (decomp.) is formed when diazoaminobenzene is allowed to stand with acetic anhydride in toluene solution (*Heusler*, Ber. 24, 4156).

Of the three diazoamino-toluenes, only diazo-*p*-aminotoluene, m.p.  $91^\circ$  is stable. The *o*- and *m*-derivatives pass immediately into the isomeric aminoazo-compounds.

Diazoamino-compounds with two different aromatic residues, or mixed diazo-amino-compounds, such as diazobenzene-*p*-aminobromo-benzene, m.p.  $91^\circ$  (*Noelling*, Ber. 20, 3012), *o*-, *m*-, *p*-dinitro-diazoamino-benzenes, m.p.  $196^\circ$ ,  $194^\circ$ ,  $228^\circ$  (*Meldola*, J. 67, 50), and diazobenzene-*p*-aminotoluene, can be obtained from the diazo-compound of either component, and the free amino-compound of the other, e.g., diazobenzene-*p*-aminotoluene can be obtained both from a phenyl diazonium salt, and *p*-toluidine, and from *p*-diazotoluene and aniline. It can also be obtained by method of formation (3) (p. 127).

*bis*-Diazobenzene-amide,  $(\text{PhN:N})_2\text{NH}$ , extremely unstable, and *bis*-diazobenzene-anilide,  $\text{PhN}=\text{N}-\text{NHPh}-\text{N}=\text{NPh}$ , lustrous yellow leaflets, exploding feebly at  $80-81^\circ$  in a capillary tube, have been prepared by method (4) (*Pechmann*, Ber. 27, 703, 899; *Bamberger*, Ber. 27, 2597; *Vignon*, C.r. 140, 91).

**MIXED FATTY-AROMATIC DIAZOAMINO-COMPOUNDS.** Diazobenzene-methyl-amide, methyl-phenyl-triazene,  $\text{PhN:N} \cdot \text{NHMe}$ , colourless plates, m.p.  $37^\circ$ , is prepared by the action of magnesium methyl iodide on phenyl azide. It volatilises with steam without decomposition. With acids it breaks down into aniline, nitrogen, and methyl esters, such as methyl chloride, methyl acetate, or methyl benzoate. It combines with phenyl isocyanate to give a substituted urea, m.p.  $104^\circ$ , which breaks down with  $\text{HCl}$  into phenyl-diazonium chloride and methyl-phenyl-urea. Cupro-methyl-phenyl-triazene,  $\text{PhN}_2\text{CuMe}$ , crystallises in orange-red prisms, m.p.  $187^\circ$  (decomp.) Acetyl-methyl-phenyl-triazene,  $\text{PhN:N} \cdot \text{N}(\text{COMe})\text{Me}$ , m.p.  $35^\circ$  (*Dimroth*, Ber. 38, 678). Diazobenzene-ethyl-amide, colourless crystals, m.p.  $31^\circ$ . Diazobenzene-ethyl-hydrazide,  $\text{PhN:N} \cdot \text{N}_2\text{H}_2\text{Et}$ , is an unstable oil, obtained from phenyl-diazonium chloride, and ethyl-phenyl hydrazine. The position of the ethyl group is uncertain. It was the first compound containing a 4-membered *N*-chain to be prepared (*E. Fischer*, Ber. 43, 3500). *p*-Tolyl-methyl-triazene,  $\text{CH}_3\text{C}_6\text{H}_4\text{N:N} \cdot \text{NHMe}$ , m.p.  $81.5^\circ$  (*Dimroth*, Ber. 40, 2397). Diazobenzene-dimethylamine,  $\text{PhN}=\text{N} \cdot \text{NMe}_2$ , is a pale-yellow oil (*Baeyer*, Ber. 8, 143). Diazobenzene-piperidine,  $\text{PhN}=\text{N} \cdot \text{NC}_4\text{H}_{10}$ , m.p.  $43^\circ$ . Diazopiperidines are useful in the preparation of fluoro-compounds (p. 49).

Benzene-diazocyanamide, phenyl-cyano-triazene,  $\text{PhN:N} \cdot \text{NHCN}$  or  $\text{PhNH} \cdot \text{N:N} \cdot \text{CN}$ , forms colourless leaflets, deflagrating at  $72^\circ$ . Its potassium salt is obtained when an alcoholic solution of phenyl azide is heated with potassium cyanide. When treated with acids it decomposes into the diazo-hydrate and urea:



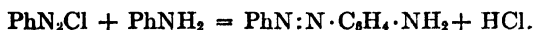
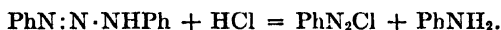
Methyl-phenyl-cyano-triazene,  $\text{PhMeN:N:NCN}$ , m.p.  $69-70^\circ$ , is formed by methylation of the potassium salt referred to above. Acids decompose it into methylaniline, nitrogen, and cyanic acid (*Wolff*, Ber. 37, 2374).

*bis*-Diazobenzene-methylamine,  $(\text{PhN}=\text{N})_2\text{NMe}$ , bright yellow needles, melts at  $112^\circ$ . *bis*-Diazobenzene-ethylamine, m.p.  $70^\circ$  (*Goldschmidt*, Ber. 22, 934).

**REACTIONS OF THE DIAZOAMINO-COMPOUNDS.** 1. Those diazoamino-compounds which have a replaceable hydrogen atom in the para-position to the  $\text{NH}$ -group, have the remarkable power of changing into isomeric *p*-aminoazo-compounds. In the aminoazo-compounds produced, the amino-group is in the *p*-position to the bond linking the benzene rings (p. 139):



This change takes place within a few days in the presence of a small quantity of a salt of aniline, but at 50° and in the presence of an excess of aniline as well as a little aniline salt, the change occurs in 2 hours. The rate of the isomerisation is proportional to the strength of the acid of which the aniline salt is used (*Goldschmidt*, Ber. 29, 1899). It is essential that an acid should be present. The reaction occurs with dilute hydrochloric, acetic, or formic acid, and even with calcium chloride, though the yield is poor when neither aniline nor a salt of aniline is present (*Rosenhauer*, Ber. 61, 392). This change was formerly regarded as a rearrangement, but the first step actually consists of the decomposition of the diazoaminobenzene into diazonium chloride and aniline, brought about by the hydrochloric acid of the aniline hydrochloride. Under the prevailing conditions the nuclei of these two compounds unite and form aminoazobenzene:



It appears from this mechanism for the reaction that only a small quantity of aniline hydrochloride or hydrochloric acid would be needed, since it is continuously regenerated. Benzene-diazoaminoazobenzene,  $\text{PhN:NC}_6\text{H}_4 \cdot \text{NH} \cdot \text{N}_2\text{Ph}$ , is a by-product in the second stage of the reaction, which shows that the diazonium salt couples with amino-azobenzene as well as with aniline (*Earl*, Ber. 63, 1666; *Rosenhauer*, Ber. 64, 1438).

2. Diazoamino-benzenes react with acid anhydrides, the hydrogen of the imino-group being replaced by an acyl-group (see benzene-diazoacetanilide, p. 129).

3. They react with phenyl isocyanate with formation of substituted ureas. The applications of this reaction are discussed on p. 128.

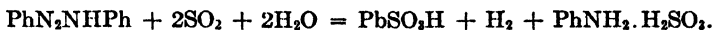
4. In the above reactions, the diazoamino-compound is not decomposed. It is, however, readily decomposed by mineral acids into the components from which it is synthesised, *viz.*, diazonium salts (or their products of decomposition) and salts of the bases which are combined with the diazo-residue. Hence, nitrous acid in the presence of acids converts them completely into diazonium salts. This method is not suitable for the determination of the constitution of asymmetrical diazoamino-compounds, as it may give ambiguous results. For example, benzenediazoamino-*p*-toluene gives a mixture of aniline, *p*-toluidine, phenol, and *p*-cresol when treated with dilute sulphuric acid. The reaction between diazoamino-compounds, and particularly of diazo-piperidines, with conc. hydrofluoric acid has been used by *Wallach* (Ann. 243, 220) for the synthesis of fluorobenzenes (p. 49).



5. The diazoamino-compounds are decomposed by boiling water giving phenols and bases.

6. Attempts to reduce the diazoamino-compounds to hydrazoamino-compounds have not been successful. Decomposition into a phenylhydrazine and an amine occurred.

7. When boiled with an alcoholic solution of sulphur dioxide, the diazo-group is replaced and sulphonic acids are formed:



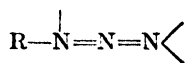
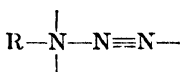
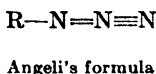
### (l) Diazohydroxyamino-compounds

These compounds are formed (1) by the action of  $\beta$ -alkyl- and  $\beta$ -aryl-hydroxylamines on diazo-compounds (with oximes, similar compounds are obtained); (2) by the action of nitroso-benzenes on phenylhydrazines, hydrogen being liberated. If  $\alpha$ -alkylated phenylhydrazines are used in this reaction, analogues of the azoxy-compounds such as  $\text{PhN}(\text{Me})\text{N}:\text{N}(\text{:O})\text{Ph}$  (p. 133) are formed (*Bamberger*, *Ber.* 32, 1546; *Bresler*, *Ann.* 353, 228).

**Diazohydroxy-amino-benzene**,  $\text{PhN}_2 \cdot \text{N}(\text{OH})\text{Ph}$ , m.p.  $127^\circ$ , crystallising in yellowish needles with a silky lustre, is obtained from nitrosobenzene and phenylhydrazine, or from a diazonium salt and phenylhydroxylamine. **Benzene-diazohydroxy-aminomethane**,  $\text{PhN}_2 \cdot \text{N}(\text{OH})\text{Me}$ , m.p.  $70^\circ$ , is formed from  $\alpha$ -methyl-hydroxylamine and diazonium chloride (*Bamberger*, *Ber.* 30, 2278). **Benzene-diazohydroxy-phenyl-methyl-amide**,  $\text{Ph}(\text{N}_2\text{O}) \cdot \text{NMePh}$ , m.p.  $72^\circ$ , is obtained from nitrosobenzene and  $\alpha$ -methyl-phenylhydrazine (p. 150). It volatilises with steam and is reduced to benzene-diazo-phenyl-methyl-amide and other substances (*Bamberger*, *Ber.* 32, 3554). For other diazohydroxy-amino compounds see *Gebhard*, *Thompson*, *J.* 85, 767.

### (m) Aryl Azides or "Diazoimino"-compounds

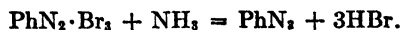
The aryl azides, e.g., phenyl azide,  $\text{PhN}_3$ , are aryl esters of hydrazoic acid,  $\text{N}_3\text{H}$ . They were formerly referred to as "diazoimido-compounds" or "diazoimides" on account of their genetic relationship to the aromatic diazo-compounds. The azide-group was formerly written as a 3-membered ring, but it is now regarded as an open chain of three nitrogen atoms. Reasons for this are given in Vol. I, p. 251, in connection with the aliphatic diazo-compounds, which resemble closely the compounds now to be described, as far as structure is concerned. X-ray photographs of crystalline sodium azide,  $\text{NaN}_3$ , have shown that the three nitrogen atoms of the azide anion are arranged in a straight line (see *Angeli*, *Atti R. Accad. Lincei* [6] 5, 732). *Angeli's* formula gives the central N atom five valency bonds, whilst the octet theory indicates the presence of only four bonds, which may be arranged in two different ways; both these states may exist (see p. 116 diazonium compounds).



Octet formulae

For the structure of organic azides see *Sidgwick*, *Trans. Faraday Soc.* 30, 801.

**Methods of formation.**—1. By the action of ammonium hydroxide on diazonium perbromides



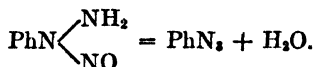
The diazonium cation combines with  $\text{NH}_3$  to give diazobenzene amide; this is then oxidised by the free bromine of the anion to phenyl azide (*cf.* 7, p. 132).

2. By the action of hydroxylamine on diazonium salts (*Mai*, Ber. 25, 372; *Curtius*, Ber. 26, 1271):



Salts of hydroxylamine-disulphonic acid have sometimes been used instead of hydroxylamine itself (*Kupe*, Ber. 33, 3408).

3. By the action of sodium nitrite on phenylhydrazine hydrochloride. Nitroso-phenylhydrazines are first formed; these rearrange, water being eliminated and phenyl-azides being formed (*Angeli*, Atti. R. Accad. Lincei [6] 5, 732; *Dimroth*, Ber. 35, 1032).

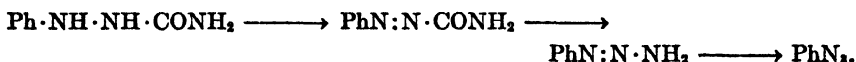


4. By the interaction of phenylhydrazine and a diazonium salt; for mechanism see below (*Griess*, Ber. 20, 1528; *Limpricht*, Ber. 21, 3415; *Wohl*, Ber. 33, 2741; *Stollé*, J. pr. 66, 336).

5. Hydrazine and diazonium sulphate react to give phenyl azide and ammonia, aniline and hydrazoic acid being by-products. These reactions are explained by the intermediate formation of  $\text{PhN}=\text{N}-\text{NHNH}_2$ , which, however, has not been isolated; cf. buzylene compounds, p. 165 (*Noelting*, Ber. 26, 88; *Curtius*, Ber. 26, 1271).



6. When  $\beta$ -phenyl-semicarbazide (p. 158) is oxidised by  $\text{NaOCl}$  phenyl azo-carboxyl-amide is the first product. This amide undergoes a Hofmann rearrangement into diazobenzene amide, and the latter is oxidised to phenyl azide:



A number of substituted phenyl-semicarbazides react in a similar way (*Darapsky*, Ber. 40, 3035).

7. By the oxidation of diazobenzene amide (p. 128) with  $\text{KOBBr}$  or ammoniacal silver nitrate. This reaction corresponds to the oxidation of hydrazones to aliphatic diazo-compounds (*Dimroth*, Ber. 40, 2388).

8. By digesting aliphatic acidyl-phenyl-nitroso-hydrazines with alkali; acidyl-aryl-hydrazines are by-products (*Ponzio*, Gazz. 45, II, 12).

Phenyl azide,  $\text{C}_6\text{H}_5\text{N}_3$ , b.p. (16 mm.)  $56^\circ$ , is a yellow oil with a stupefying odour. It explodes when heated at ordinary pressure.

*o*-, *m*-, *p*-Nitrophenyl azides,  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_3$ , m.p.  $52^\circ$ ,  $55^\circ$ , and  $71^\circ$ . Picryl azide, m.p.  $93^\circ$ , obtained from picryl chloride and sodium azide, is not explosive (*Schrader*, Ber. 50, 777). *p*-Chlorophenyl azide, b.p. (20 mm.)  $96^\circ$ . *p*-Bromophenyl azide, m.p.  $57-58^\circ$  (*Bergmann*, Z. physikal. Chem. Abt. B 19, 389). *p*-Aminophenyl azide,  $\text{NH}_2\text{C}_6\text{H}_4\text{N}_3$ , m.p.  $62^\circ$ .

*p*-bis-Triazobenzene, *p*-phenylene-bis-diazo-imide,  $\text{N}_3\text{C}_6\text{H}_4\text{N}_3$ , forms bright yellow plates, m.p.  $83^\circ$ , and has been prepared from acetyl-*p*-phenylene diamine by the following series of reactions (*Silberrad*, J. 89, 167, 170):



**1,3,5-Trinitro-2,4,6-tris-triazobenzene**,  $(\text{NO}_2)_3\text{C}_6(\text{N}_3)_3$ , m.p.  $131^\circ$ , obtained from 2,4,6-trichlorobenzene by means of the 1,3,5-trinitro-product with sodium azide, is a powerful explosive (*Turek, Chim. et Ind., 1932*). **tris-Triazomesitylene**,  $(\text{CH}_3)_3\text{C}:(\text{N}_3)_3$ , m.p.  $50^\circ$ , is obtained by the action of sodium azide on tri-amino-mesitylene trihydrochloride (p. 110) followed by the action of HCl and  $\text{HNO}_3$  (*Morgan, Davies, J. 123, 228*).

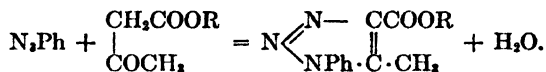
**5-tert Butyl-4,6-dinitro-2-azido-1,3-xylene, azide musk**, m.p.  $89^\circ$ , is obtained from *p*-butyl xylidine (m.p.  $32^\circ$ ) by diazotisation and nitration. The corresponding toluene compound melts at  $146^\circ$ .

**Reactions of the aryl azides.**—1. On boiling with HCl they decompose into nitrogen and chloroaniline (*Griess, Ber. 19, 313*). 2. On boiling with  $\text{H}_2\text{SO}_4$ , they break down into nitrogen and aminophenols (*Friedländer, Ber. 27, 192*). 3. On boiling with alcoholic potash, aryl azides which are nitrated in the *o*- or *p*-position partly decompose into nitrophenols and hydrazoic acid. 4. When heated alone, the *o*-nitrated azides decompose into nitrogen and benzofuroxanes.

5. With methyl magnesium iodide and phenyl magnesium bromide, phenyl azide gives diazoamino salts (p. 127).

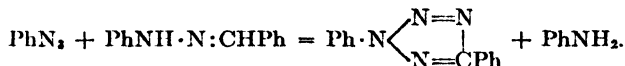
6. It combines with potassium cyanide to form phenyl cyanotriazene (p. 129).

7. It adds on to acetylene dicarboxylic ester, and reacts with  $\beta$ -ketocarboxylic and malonic esters with elimination of water or alcohol, five-membered heterocyclic ring systems of the triazole group (Vol. IV) being formed (*Dimroth, Ber. 35, 4041*):



The same reactions are encountered with aliphatic diazo-compounds.

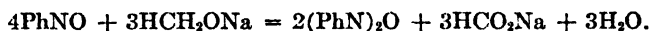
8. By condensing phenyl azide with benzaldehyde-aryl-hydrazones, *tetrazoles* are obtained (Vol. IV) (*Dimroth, Ber. 40, 2402*):



9. For the addition reactions of phenyl azide with cyclopentene and cycloheptene, see *Alder, Ann. 501, 1*.

### (n) Azoxy-compounds\*

**Methods of formation.**—1. By reducing nitro- or nitroso-compounds with alcoholic or methyl alcoholic potash (*Lachman, Am. 24, 1178*; *Reissert, Ber. 42, 1364*):



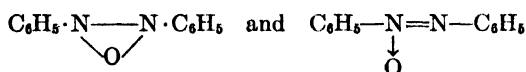
Sodium amalgam and ethyl alcohol, zinc dust in alcoholic  $\text{NH}_3$ ,  $\text{As}_2\text{O}_3$  in alcoholic solution (Ger. Pat. 77,563), and zinc oxide and sodium hydroxide also reduce nitro- to azoxy-compounds. 2. By oxidising azo-compounds with  $\text{H}_2\text{O}_2$  in acetic acid. They may also be obtained by oxidising amines, though the yield is poor (*Bamberger, Ber. 36, 3805*; *Angeli, Atti. Accad. Lincei 24, I, 1185*). They may be obtained by spontaneous oxidation of *N*-phenyl-hydroxylamine in air, in which case nitroso-benzene is first formed and unites with the unchanged phenyl-hydroxylamine to give azoxybenzene. For a discussion of steric hindrance in this reaction see p. 68. 3. Azoxybenzene and its nitro-derivatives are obtained from nitro-compounds, such as *m*-dinitrobenzene, by the action of phenyl-hydroxylamine

\* See *H. E. Bigelow, Chemical Reviews, 1931, 9, 117*.

(*Meisenheimer*, Ber. 53, 358). 4. Benzyl alcohol reduces nitrobenzenes to azoxybenzenes, being itself oxidised to benzaldehyde and benzoic acid (*Suter*, Am. 50, 2733).

*History*.—Azoxybenzene was discovered in 1864 by *Alexejev* who reduced alcoholic nitrobenzene with sodium amalgam (Bull. 6, 324; *Glaser*, Z. f. Chem., 1866, 309; *Wreden*, Ber. 6, 558; *Limpricht*, Ber. 18, 1420).

*Constitution*.—Instead of the symmetrical formula *Angeli* (Gazz. 46, II, 67) first suggested the asymmetrical formula  $\text{Ph} \cdot \text{N}(\text{O}) : \text{N} \cdot \text{Ph}$  as a logical consequence of the formula assigned by him to phenyl-nitramine (p. 111). If this formulation is correct, isomeric forms of asymmetrical azoxy-compounds would be expected, and two isomers of compounds like monobromoazoxybenzene,  $\text{BrC}_6\text{H}_4 \cdot \text{N}(\text{O}) : \text{N} \cdot \text{Ph}$  and  $\text{BrC}_6\text{H}_4 \text{N} : \text{N}(\text{O}) \cdot \text{Ph}$ , have actually been isolated by oxidising the asymmetrical azo-compounds with  $\text{H}_2\text{O}_2$  as well as by method 2, by condensing nitroso-compounds with phenyl-hydroxylamine in the presence of a little caustic alkali. Of the two possible formulae of azoxybenzene:



only the asymmetrical one will account for such isomerism. Further, isomerism would be expected owing to the different spatial arrangement of the groups attached to the N-atoms (*Müller*, Ann. 495, 132):



The *iso*- differ from the *n*-forms in being less soluble in ligroin. For the absorption spectra of azoxy-compound see *Auwers*, Ann. 499, 123.

*Reactions*.—1. When reduced by heating with iron filings they give azo-compounds; with ammonium sulphide, they give hydrazo-compounds, and with acidic reducing agents amino-compounds are formed. All these products arise from the decomposition and reactions of the hydrazo-compounds first formed.

2. They undergo an interesting rearrangement into hydroxy-azo-compounds when gently warmed with conc. sulphuric acid (*Wallach*, Ber. 13, 525; cf. *Bamberger*, Ber. 33, 3192; *Lachmann*, Am. 24, 1178; *Parsons*, J. Am. Chem. Soc. 58, 268).

3. With magnesium methyl iodide, or magnesium and magnesium iodide, azoxybenzenes are first reduced to azobenzenes and then to hydrazobenzenes (*Gilman*, Rec. 50, 522).

**Azoxybenzene**,  $\text{PhN}(\text{O}) : \text{NPh}$ , *n*-, or *cis*-, form, m.p.  $36^\circ$ ,  $\mu$  1.70, and *iso*, or *trans*-, form, m.p.  $86^\circ$ ,  $\mu$  4.87. The latter is a by-product in the reduction of nitrosobenzene with alcoholic soda and is separated from the normal form by means of ligroin (*Reissert*, Ber. 42, 1367). When heated it changes into the normal form. This is insoluble in water, readily soluble in alcohol and ether. When dis-

tilled, it is partly converted into azo-benzene and aniline, and when treated with conc.  $\text{H}_2\text{SO}_4$  into *p*-hydroxy-azobenzene and other products (*Knipscheer*, *Rec.* 22, 1).

Azoxybenzene reacts with benzene and aluminium chloride giving benzene-azo-diphenyl,  $\text{PhN}_2\text{C}_6\text{H}_4\text{Ph}$ , and diphenyl-azo-diphenyl,  $\text{Ph}\cdot\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\cdot\text{Ph}$  (*Bandrowski*, *C.* 1904, I, 1491).

*o,o*-Dichloro-azoxybenzene, m.p.  $57^\circ$  and  $93^\circ$  (*Müller*, *Ann.* 493, 168; 495, 135).

*o*-Nitro-azoxybenzene, m.p.  $49^\circ$ ; *m*-Nitro-azoxybenzene, m.p.  $120$ – $121^\circ$  and  $86$ – $88^\circ$  (*Meisenheimer*, *Ber.* 53, 364); *p*-nitro-azoxybenzene, m.p.  $149^\circ$  and  $153^\circ$  (*Angeli*, *Atti. Accad. Lincei* 20, II, 170). The *o*-compound is reduced to phenyl-aznitroso- and phenyl-azimino-benzene (*Werner*, *Ber.* 32, 3263). For the further nitration of the *o*- and *p*-compounds see *Angeli*, *loc. cit.*

*as*-3,5-Dinitro-1-azoxybenzene, m.p.  $171$ – $173^\circ$  is obtained from 1,3,5-trinitrobenzene and phenyl hydroxylamine (*Meisenheimer*, *Ber.* 53, 358). *o,o'*-Dinitro-azoxybenzene, m.p.  $175^\circ$  (*Bamberger*, *Ber.* 36, 3813). *sym-p,p'*-Dinitro-azoxybenzene, m.p.  $192^\circ$  is obtained by oxidation of *p,p'*-dinitro-azobenzene. *sym-m,m'*-Dinitro-azoxybenzene, m.p.  $146.5^\circ$ , is obtained from *m*-dinitrobenzene (*Willgerodt*, *Ber.* 25, 608; *Brand*, *Ber.* 38, 4013). *Iso*-compounds, *o*-, *m*-, *p*-, m.p.  $81^\circ$ ,  $89^\circ$ ,  $85$ – $86^\circ$  (*Müller*, *Ann.* 495, 135). Trinitro-azoxybenzenes are obtained from azoxybenzene (*Klinger*, *Ann.* 255, 310).

*o*-Hydroxylamino-azoxybenzene,  $\text{NHOH}[2]\text{C}_6\text{H}_4\text{N}:\text{N}(\text{O})\cdot\text{Ph}$ , m.p.  $118^\circ$ , is produced from *o*-nitro-azoxybenzene by catalytic reduction (*Cusmano*, *Gazz.* 51, I, 65).

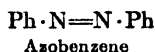
*sym-m*-Diamino-azoxybenzene, azoxy-aniline, m.p.  $147^\circ$  (*Meldola*, *J.* 69, 7). *p*-Tetramethyl-diamino-azoxybenzene, m.p.  $243^\circ$  is obtained from nitrosodimethylaniline.

**POLY-AZOXY-COMPOUNDS:**  $\text{Ph}\cdot\text{N}(\text{O}):\text{N}\cdot\text{C}_6\text{H}_4\text{N}:\text{N}(\text{O})\cdot\text{Ph}$ , m.p.  $168^\circ$  ( $\alpha$ -form).  $\text{Ph}\cdot\text{N}\cdot\text{N}(\text{O})\cdot\text{C}_6\text{H}_4\text{N}(\text{O}):\text{N}\cdot\text{Ph}$ , m.p.  $155^\circ$  ( $\beta$ -form),  $\text{Ph}\cdot\text{N}(\text{O}):-\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{O}):\text{N}\cdot\text{Ph}$ , m.p.  $148^\circ$  ( $\gamma$ -form) (*Angeli*, *Atti. Accad. Lincei* 22, I, 844).

**AZOXYTOLUENES**, *o*-, *m*-, *p*-, m.p.  $59^\circ$  and  $82^\circ$ ,  $38^\circ$  and  $89^\circ$ ,  $76^\circ$  and  $83$ – $85^\circ$ . 2,6-Dinitro-4-azoxytoluene, m.p.  $212$ – $213^\circ$ , is formed, together with the corresponding 4-amino-toluene, m.p.  $168$ – $169^\circ$ , when 2,6-dinitro-4-hydroxylamino-toluene is boiled with  $\text{HCl}$  (*Anschütz*, *Ber.* 48, 152).

### (o) Azo-compounds

Like the diazo-compounds, the azo-compounds contain a group of two nitrogen atoms. In the former, this  $\text{N}_2$  group is combined with one benzene ring and an inorganic residue; in the azo-compounds it links two benzene rings together, or one benzene ring and an aliphatic radical:



On this account, the azo-compounds are much more stable than the diazo-compounds, and they react without elimination of nitrogen.

The diazobenzene cyanides, the derivatives of benzeno-azo-carboxylic acids (p. 121) and other similar compounds, are intermediate links between the diazo- and the azo-compounds.

**Classification and nomenclature.**—The true aromatic azo-compounds are distinguished as symmetrical when they have two identical aromatic residues, and asymmetrical when the two residues are different. Azo-compounds in which the azo-group links an aromatic to an aliphatic residue are called mixed azo-compounds.

The names of asymmetrical azo-compounds are composed of the

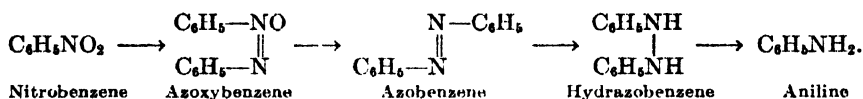


names of the two compounds in each of which the azo-group replaces one H-atom, separated by the word azo; thus,  $\text{Ph} \cdot \text{N}=\text{N} \cdot \text{C}_6\text{H}_4\text{NMe}_2$  is called benzene-azo-dimethylaniline;  $\text{Ph} \cdot \text{N}=\text{N} \cdot \text{Me}$  is called benzene-azo-methane. If the benzene residues contain substituents, the positions are designated by the numbers 2 to 6 in the one, and 2' to 6' in the other, 1 and 1' being assigned to the azo-group.

*bis-Azo-* and *tris-azo-*compounds, containing the azo-group, respectively, twice or thrice have been prepared by Wallach (Ber. 15, 2812).

*Methods of formation.*—1. Azo-compounds are obtained by reduction of nitro-compounds in alkaline solution, azoxy-compounds (p. 133) being intermediate products. In acid solution amines, the final reduction products of nitro-compounds, are almost invariably formed. The following reducing agents may be used: zinc dust and alcoholic potash or soda, or caustic soda, or ammonia (Noelting, Ber. 21, 3139); sodium or magnesium amalgam and alcohol (Evans, Am. 26, 1161);  $\text{SnCl}_2$  in  $\text{NaOH}$  (Witt, Ber. 18, 2912). In addition, electrolytic reduction (Elbs, Z. Elektrochem. 5, 108; Ger. Pats. 108,427, 121,819, and 121,900) and catalytic reduction with hydrogen in the presence of  $\text{Ti}$ -powder (Henke, J. Phys. Chem. 26, 631) have been used.

By more complete reduction hydrazo-compounds are formed in addition to the azo-compounds, and finally amines are produced. Azobenzene is the middle member in the series of reduction products of nitrobenzene, if *N*-phenyl-hydroxylamine is disregarded:



2. Azo-compounds may also be prepared by heating azoxy-compounds with iron filings.

3. They may be obtained by oxidation of (a) hydrazo-compounds (p. 143) and (b) primary amines in alkaline solution simply by the action of air (Bacovescu, Ber. 42, 2938) or, more readily by the action of  $\text{KMnO}_4$  (Glaser, Ann. 142, 364),  $\text{K}_3\text{Fe}(\text{CN})_6$ , or  $\text{NaOBr}$ .

The following reactions also give rise to azo-compounds:

4. The action of nitroso-benzenes (p. 66) on anilines.

5. The action of ammoniacal cuprous solutions on diazonium salts (p. 125).

6. The rearrangement of certain diazoamino-compounds into aminoazo-compounds (p. 140).

7. The action of diazo-salts on (a) tertiary aromatic amines, (b) *m*-diamines, (cf. p. 139), (c) phenols and phenol ethers.

8. The action of diazo-compounds which couple readily (those of nitraniline, dinitro- and trinitro-anilines) on aromatic hydrocarbons, such as mesitylene.

Methods 6 and 7 lead to the amino- and hydroxy-compounds of azo-hydrocarbons, some of which are important in the dyeing industry.

*Mixed azo-derivatives* are frequently obtained by combining diazo-salts with suitable aliphatic compounds which contain easily replace-

able hydrogen atoms united to carbon, or with heterocyclic compounds, such as pyrrole, pyrazole, *etc.* Some diazo-compounds, which couple very readily (*cf.* 8) react even with olefines, such as butadiene, *etc.* (*Dimroth*, Ber. 50, 1534).

*Properties.*—The azo-compounds are more highly coloured than the pale-yellow or colourless azoxy-compounds. They combine with acids with great difficulty unless they contain a basic amino-group (*Hantzsch*, Ber. 42, 2130). They can be directly chlorinated, nitrated, or sulphonated. Reducing agents either convert them into hydrazo-compounds (p. 143), or the double bond is broken and amines are formed. The latter reaction serves to establish their constitution. Oxidising agents, such as  $H_2O_2$ , convert them into azoxy-compounds.

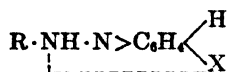
As far as is known, the azo-hydrocarbons possess the *trans*-configuration with respect to the  $-N=N-$  group; this is indicated by measurements of dipole moments. Azobenzene, for example, has a zero dipole moment (*Bergmann*, Ber. 63, 2572).

### Symmetrical Azo-compounds

**Azobenzene**,  $C_6H_5N=NC_6H_5$ , m.p.  $68^\circ$ , b.p.  $293^\circ$ , was discovered by Mitscherlich in 1834. It forms orange-red, rhombic crystals, readily soluble in alcohol and ether, and sparingly soluble in water. It is obtained from nitrobenzene, aniline, hydrazobenzene, or azoxybenzene by the methods given above. It is also obtained by the action of atmospheric oxygen on potassium-aniline, and from bromylaniline ( $PhNBr_2$ ) by the action of sodium. When reduced with tin and hydrochloric acid it is converted into benzidine. Hydrazibenzene is first formed in this reaction, but rearranges. With metallic potassium, azobenzene forms a brownish-violet addition product

similar to quinhedrone in character, 
$$\begin{array}{c} Ph \cdot NK \cdot NK \cdot Ph \\ \searrow \quad \nearrow \\ Ph \cdot N \equiv N \cdot Ph \end{array} \quad (Emmert, \text{ Ber. 54, 204}).$$

Azobenzene is attacked by methyl alcoholic HCl, simultaneous reduction and chlorination occurring (*Auwers*, Ann. 367, 309). With benzene and aluminium chloride in the presence of HCl, amino-diphenyl,  $PhC_6H_4NH_2$ , is formed (*Pum-merer*, Ber. 55, 3095). Azobenzene combines with benzene-sulphonic acid to give N-phenyl-sulphone-hydrazobenzene, m.p.  $107^\circ$ . When heated with  $CS_2$  it yields mercapto-thiazole (*cf.* thiazoles, Vol. IV) (*Jacobsen*, Ber. 24, 1403). Organo-magnesium compounds reduce it to hydrazobenzene; for the mechanism of this reaction see *Gilman*, Am. 48, 2004. For the electrochemical oxidation of azobenzene, see *Fichter*, Helv. 4, 1000. Quinoid salts of azobenzene, of the type



have been studied by *Hantzsch* (Ber. 63, 1760).

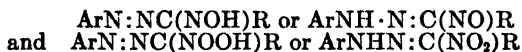
When azobenzene is nitrated, nitro-azoxybenzenes are chiefly formed, oxidation going on simultaneously. *o*-, *m*-, *p*-Nitro-azobenzenes, m.p. 71, 96, and  $135^\circ$ , are prepared by acting on the three nitro-nitrosobenzenes with aniline, or the three nitranilines with nitrosobenzene (*Bamberger*, Ber. 36, 3811, 3818).

2,4-Dinitrobenzene-azobenzene, m.p.  $117^\circ$ , is obtained from the corresponding hydrazobenzene (p. 143) by oxidation. *m,m'*- and *p,p'*-Dinitro-azobenzenes, m.p.  $153^\circ$  and  $223^\circ$ , the latter forming orange-red laminae, are obtained from

*p*-nitraniline by the action of bleaching powder in aqueous suspension (Green, J. 99, 1960). Cf. Werner, Ber. 32, 3256. Trinitro-azobenzene see Werner, *ibid.* 2, 4, 6, 4'-Tetranitro-azobenzene, m.p. 163-164° (Ciusa, Gazz. 41, I, 688). *sym*-Hexanitro-azobenzene, m.p. 215° (Leemann, Ber. 41, 1297). *o*-Nitroazo-compounds give phenyl-azimide oxides and phenyl- $\psi$ -azimides on reduction (Bamberger, Ber. 36, 3822).

**AZOTOLUENES.** Benzene-azo-*o*-toluene, Ph·N:N·C<sub>6</sub>H<sub>4</sub>Me, b.p. (4 mm.) 156-158°, benzene-azo-*p*-toluene, m.p. 71-72°, obtained from nitroso-benzene and *o*- and *p*-toluidine, resp., are reduced by zinc dust in alcoholic acetic acid solution to benzene-hydrazo-*o*- and -*p*-toluene, resp., m.p. 101-102°, and 87-88°, resp. (Ritter, Am. 52, 281). *o*-, *m*-, and *p*-Azotoluenes, m.p. 157°, 55°, and 143° (Schultz, Ber. 17, 463; Klinger, Ber. 18, 2551). Azoxylenes and azo-trimethyl-benzenes are also known.

**MIXED AZO-COMPOUNDS.** Benzene-azomethane, PhN=NMe, b.p. about 150°, and benzene-azoethane, PhN:NEt, m.p. about 180°, are liquids with a peculiar odour, obtained by oxidising the corresponding hydrazines with mercuric oxide; small quantities of benzene-azoethane are also obtained by the action of phenylhydrazine on formaldehyde (Stobbe, Ber. 47, 578). Sulphuric acid, or NaOEt converts benzene-azoethane into the isomeric acetaldehyde-phenylhydrazone, PhNH·N:CHCH<sub>3</sub> (Fischer, Ber. 29, 1794; Bamberger, Ber. 36, 56). With amyl nitrite and NaOEt both benzene-azoethane and acetaldehyde-phenylhydrazone give benzene-acetaldoxime, PhN:NC(NO)Me. In compounds of the type



the desmotropic relations between azo- and hydrazone-forms are closer than in the simple mixed azo-compounds. These classes of compounds designated as benzene-azo-aldoximes or nitroso-phenylhydrazones, and as benzene-azo-nitronic acids or nitro-phenylhydrazones, respectively, will be dealt with later, after the phenylhydrazine derivatives (p. 161) and together with the related amidrazones and formazyl-compounds.

Diazo-salts combine with compounds with reactive CH<sub>2</sub>-groups to form mixed azo-compounds, such as benzene-azo-acetoacetic ester, PhN:NCH(COCH<sub>3</sub>)COOR, and benzene-azo-nitromethane, PhN:N·CH<sub>2</sub>NO<sub>2</sub>, which apparently rearrange immediately into the desmotropic hydrazone forms PhNH·N:C(COCH<sub>3</sub>)COOR and PhNH·N:CHNO<sub>2</sub>. For the structure of benzene-azo-aminocrotonic ester formed from aminocrotonic ester and a phenyl-diazonium solution, see Prager, Ber. 35, 1862.

Phenyl-azo-carboxyl amide, Ph·N:N·CONH<sub>2</sub>, orange-red needles, m.p. 114°, is an oxidation product of  $\beta$ -phenyl-semicarbazide (p. 158). Phenyl-azo-carboxyl anilide, PhN:NCO·NHPh, m.p. 122°, is obtained from 1,4-diphenyl-semicarbazide (p. 158). Azo-hydroxamic acid, PhN:N·CO·NHOH, is produced from an aryl-diazonium salt by the action of potassium-trinitromethane, an addition product, and possibly nitrocarbonyl-arylnitroso-hydrazine being intermediate products. Phenyl-azo-formhydroxamic acid, PhN:N·CONHOH, colourless needles, m.p. 84-85° gives, when nitrated, *p*-nitrophenyl-azo-formhydroxamic acid, yellowish needles, m.p. 165-166°. *p*-Tolyl-azo-formhydroxamic acid, m.p. 102°. When heated with caustic alkalis these compounds decompose into aryl azides and CO<sub>2</sub> (Ponzo, Gazz. 45, II, 12; 46, II, 56).

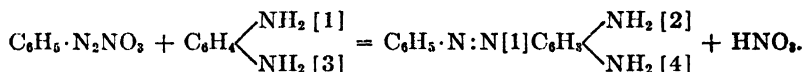
Certain other substances may also be regarded as mixed azo-compounds, e.g., the diazo-cyanides (p. 121), diphenyl-sulpho-carbazone and -carbodiazone (p. 160), benzoyl-diazobenzene (p. 303), and many azo-compounds prepared by combining diazo-salts with heterocyclic compounds, such as pyrrole, pyrazole, etc.; also compounds produced by the action of *p*-nitro- and *o*,*p*-dinitro-phenyl-diazo-hydroxides on aliphatic olefines, such as butadiene, and isoprene, e.g., *p*-nitrophenyl-azobutadiene, NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>·N:N·CH:CH·CH:CH<sub>2</sub> (Meyer, Ann. 398, 66; Ber. 47, 1741). For azo-ketones and azo-nitriles see Angeli, Lincei 24, I, 1185.

**AMINOAZO-COMPOUNDS.** The azo-compounds are all orange-yellow to orange-red in colour, but they are not dyestuffs. By the introduction of amino- or hydroxyl-groups in the *o*- and *p*-

position to the azo-group, *o*- and *p*-aminoazo-compounds, and *o*- and *p*-hydroxyazo-compounds are obtained, and these will dye silk and wool (*Binz*, Ber. 35, 4225). The number of azo dyestuffs is very great; some of the simplest will be mentioned here, while the most important representatives of this class from an industrial point of view will be dealt with elsewhere in this book, chiefly in the section on naphthalene derivatives. More important than the aminoazo-compounds themselves are their sulphonic acids.

*Methods of formation.*—1. From diazoamino-compounds, *e.g.*, *p*-aminoazobenzene from diazoaminobenzene (p. 126). This rearrangement is a general reaction taking place under certain conditions in the presence of acids; it proceeds almost quantitatively when an excess of aniline and a small amount of aniline hydrochloride are added, the solution being then feebly acidic. Under modified conditions, *Witt* has succeeded in obtaining also *o*-aminoazobenzene (Ber. 46, 2557). The reaction proceeds only with difficulty if the *p*-position to the amino-group in the diazoamino-compound is occupied. However, with a compound like diazoamino-*p*-toluene,  $\text{Me}[4]\text{C}_6\text{H}_4[1]\text{N}:\text{N}[1']\text{-NHC}_6\text{H}_4[4']\text{Me}$ , where methyl occupied the *p*-position to the NH group, the change can be effected by dissolving the substance in molten *p*-toluidine, adding *p*-toluidine hydrochloride and heating to 65°. In the resulting amino-azotoluene, the amino-group is in the ortho-position to the azo-group, *o*-aminoazotoluene, or 4-methylbenzeneazo-4'-methyl-2'-aminobenzene,  $\text{CH}_3[4]\text{C}_6\text{H}_4[1]\text{N}:\text{N}[1']\text{C}_6\text{H}_3[4']\text{CH}_3[2']\text{NH}_2$ , (*Noelting*, Ber. 17, 77).

2. Diazonium salts react with (a) tertiary aromatic amines, and (b) *m*-diamines, in neutral or weakly acidic solution (*Hofmann*, *Witt*, Ber. 10, 389, 654):

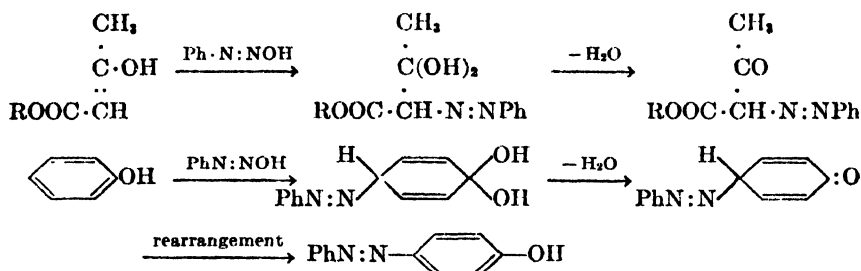


Primary and secondary monoamines in general give diazoamino-compounds most readily in neutral or acetic acid solution (*Bamberger*, Ber. 24, 2077), and these, under the conditions specified above, rearrange to aminoazo-compounds. Ring-substituted amines, however, immediately give a certain percentage of aminoazo-compounds, and in the case of *m*-substituted amines, such as *m*-toluidine, they are the chief product (*Mehner*, J. pr. 65, 401).

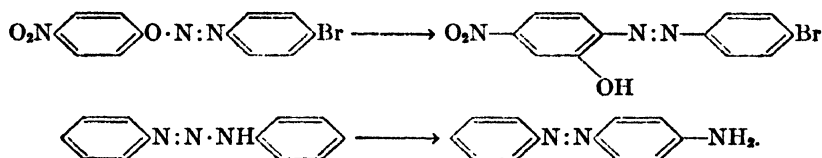
The action of phenols on diazonium salts is similar; the hydroxyazo-compounds which result will be dealt with later, in connection with the aminophenols.

*Mechanism of coupling.*—1. The simplest theory is the one put forward by *K. H. Meyer* (Ber. 47, 1741; 52, 1468), which brings all coupling reactions into a common scheme. It applies not only to the well-known coupling of the aromatic amines with phenols, aliphatic enols, and *aci*-nitro-compounds, but also to the coupling of phenol ethers and particularly to that of diolefines and aromatic hydrocarbons discovered by Meyer. In all these cases the primary process may be

regarded as the addition of the diazo-compound to a double bond. The para-coupling is an addition in the 1,4-position to the system of conjugated double bonds present in the benzene molecule. When groups like OH, NH<sub>2</sub>, etc., are attached to the double bond, as in the phenols, aromatic amines and enols, the double bond has become "active" and the addition occurs very readily. The following scheme represents the coupling of acetoacetic ester and of phenol, as given by this theory:



2. The coupling of phenols and of aromatic amines can be explained from another point of view. The first phase of the reaction may consist of an interaction between the diazonium hydroxide and the OH or NH<sub>2</sub> group leading to the formation of a diazo-phenyl ether (*Dimroth*, Ber. 41, 4012; 50, 1534), or a diazoamino-compound. Such intermediate products are known in the case of nitrophenol and aniline, and rearrange readily into azo-compounds:



Though phenol ethers and tertiary amines are incapable of forming similar intermediate products, the first attack might be directed to the methoxy- or dialkyl-amino-group and an oxonium or ammonium compound might be formed, with subsequent rearrangement into an azo-compound (*Karrer*, Ber. 48, 1398).

3. *Wieland's* view of the coupling process is explained in *Gattermann-Wieland*, Die Praxis des organischen Chemikers, 19 Auflage, 1925, p. 278.

4. In *Rosenhauer's* view (Ber. 61, 392) no true rearrangement takes place, but the change is brought about by the acid (of the aniline or other salt added) decomposing the diazoamino-benzene to benzene diazonium salt + base, followed by a nuclear coupling of these two products.

**Properties and reactions.**—The amino-azo-compounds are crystalline substances, yellow, red, or brown in colour. Most of them dissolve freely in alcohol. With acids, two isomeric series of salts are formed. The salts of the first series are yellow, unstable, and are formed by the action of an insufficient quantity of acid; with an excess of acid, or

under the influence of pressure or heat, they are readily changed to the dark violet, stable salts of the second series. These latter are probably the salts of quinone-imido-hydrazones:  $\text{PhNHN}:\text{C}_6\text{H}_4:-\text{NH}\cdot\text{HCl}$ . They are the industrial aminoazo-dyes. The salts of the first class are given the formula  $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\text{X}$  (*Hantzsch*, Ber. 41, 1171; 63, 1760).

1. The fission of the aminoazo-compounds on reduction has been mentioned above, and the significance of this reaction has been explained (*cf. Witt*, Ber. 21, 3471; *Frantzen*, J. pr. 76, 467). Some of them undergo the same decomposition when they are heated with  $\text{HCl}$  (*Wallach*, Ber. 17, 395). If  $\text{TiCl}_3$  is used as the reducing agent, the reaction proceeds quantitatively, and may be used for the volumetric determination of dyestuffs (*Knecht*, Ber. 36, 1552).

2. The aminoazo-compounds are converted by nitrous acid into diazo-compounds. By reducing the diazonium salts of *o*-aminoazo-compounds, *v-dihydrophenotetrazines* are obtained (Vol. IV).

3. *Indulines* and *eurhodines* (Vol. IV) are formed when *p*- and *o*-aminoazo-compounds, respectively, are heated with aniline hydrochloride.

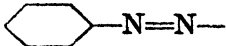
4. On oxidation the *o*-aminoazo-compounds give *pseudo-azimino-compounds*, and

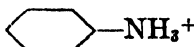
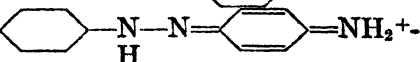
5. With aldehydes they form *amino-benzimidiazoles*.

6. The nitrates of aminoazo-compounds decompose, on heating, into free aminoazo-compounds and nitric acid. The two products react with each other, forming a diazonium nitrate and a nitro-compound of the amine (*Casale*, Gazz. 45, II, 397).

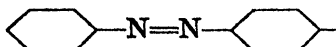
***o*-Aminoazobenzene**, forms deep red prisms with a greenish, metallic lustre, m.p.  $59^\circ$ . It is obtained by acting upon benzoyl-*o*-phenylene diamine with nitrobenzene to give *o*-benzoyl-aminoazobenzene, and decomposing this with sodium ethoxide. *Acetyl* compounds, m.p.  $126^\circ$  (*Witt*, Ber. 45, 2380).

***p*-Aminoazobenzene**,  $\text{Ph}\cdot\text{N}:\text{N}(1)\text{Ph}(4)\text{NH}_2$ , yellow flakes or needles, m.p.  $127^\circ$ , b.p. (12 mm.)  $225^\circ$ , boils without decomp. even at ordinary pressure. It can be obtained from *p*-nitroazobenzene, whilst the industrial method of manufacture is based on the rearrangement of diazoamino-benzene, the latter compound not being actually isolated (*Staedel*, Ber. 19, 1953; *Gattermann*, Ber. 21, 1633). It is oxidised by manganese dioxide and sulphuric acid to quinone. It is decomposed on reduction into aniline and *p*-phenylene diamine (p. 106).

With one mol. of  $\text{HCl}$  it forms two isomeric salts:   $\text{N}=\text{N}-$

  $\text{NH}_2+\text{Cl}^-$  is yellow, and   $\text{N}=\text{N}-\text{NH}_2+\text{H}^+$

$\text{Cl}^-$  is dark violet (*Hantzsch*, Ber. 63, 1760). In addition, salts with more than one equivalent of acid are known, the amino- and azo-nitrogen both uniting with a proton. For a discussion of azo-indicators and their changes of colour see *Hantzsch*, Ber. 41, 1171; 63, 1760; Z. anorg. Chem. 135, 1), and *Weissberger* (Z. physikal. Chem. A, 157, 65). According to Ostwald the yellow compound,

  $\text{—N=N—NH}_2$ , changes, when forming a salt, into the meriquinoid form represented above, and the solution contains the ions of the latter. The violet hydrochloride and the oxalate were formerly used as dyes, but are no longer of importance. The sulphonic acids, known as *fast yellow* or *acid yellow*, are more often used. Aminoazobenzene is manufactured in large quantities as a starting material for *bis*-azo-dyes and indulines. When oxidised with  $\text{H}_2\text{O}_2$  in acetic acid it gives the triazo-compound  $\text{PhN:N}\cdot\text{C}_6\text{H}_4\text{N:N}\cdot\text{C}_6\text{H}_4\text{N:N}\cdot\text{Ph}$ , red flakes, with a golden lustre, m.p.  $229^\circ$ , together with a *bis*-azo-monoazoxy-compound,  $\text{Ph}\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot(\text{N}_2\text{O})\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{Ph}$ , yellow crystals, m.p.  $215^\circ$ . Both substances, on continued treatment with  $\text{H}_2\text{O}_2$ , give the tri-azoxy-compound,  $\text{Ph}\cdot(\text{N}_2\text{O})\cdot\text{C}_6\text{H}_4\cdot(\text{N}_2\text{O})\cdot\text{C}_6\text{H}_4\cdot(\text{N}_2\text{O})\cdot\text{Ph}$ , golden yellow prisms, m.p.  $230^\circ$  (*Valori, Atti Accad. Lincei* **23**, II, 213).

***p*-ACETAMINO-AZOBENZENE**, m.p.  $143^\circ$ . Benzene-azo-phenyl-cyanamide,  $\text{PhN:NC}_6\text{H}_4\text{NHCN}$ , m.p.  $163^\circ$ , is obtained by the action of phenyl diazonium chloride on sodio-cyano-aniline (*Pierron, C.r.* **143**, 340). Benzene-azo-phenylglycine,  $\text{PhN:NC}_6\text{H}_4\text{NHCH}_2\cdot\text{COOH}$ , m.p.  $140^\circ$ , is obtained from phenylglycine and phenyl diazonium chloride. For the acyl derivatives of *p*-aminoazobenzene see *Mai, Ber.* **35**, 580; *Wielezyski, Ber.* **35**, 1431; *Chattaway, Proc.* **18**, 174).

*m*-Aminoazobenzene,  $\text{PhN}_2[1]\text{C}_6\text{H}_4[3]\text{NH}_2$ , m.p.  $67^\circ$ . Acetyl compound, m.p.  $131^\circ$  has been obtained from nitroso-benzene and acet-*m*-phenylene diamine (*Mills, J.* **67**, 925). Benzene-azo-*p*-dimethylaniline,  $\text{PhN:N}[1]\text{C}_6\text{H}_4[4]\text{NMe}_2$ , m.p.  $116^\circ$ . *p*-Azobenzene-trimethylammonium iodide,  $\text{PhN:NC}_6\text{H}_4\text{NMe}_3\text{I}$ , m.p.  $185^\circ$ , is obtained from the preceding compound by the action of  $\text{MeI}$ ; in contrast to the corresponding primary and tertiary amine salts it does not dye wool or silk (*Vorländer, Ann.* **345**, 308). Benzene-azo-diphenylamine, m.p.  $82^\circ$ . *o*-Aminoazotoluene,  $\text{Me}[2]\text{C}_6\text{H}_4[1]\text{N:N}[1']\text{C}_6\text{H}_3[3',4']\text{MeNH}_2$ , m.p.  $100^\circ$ , is obtained from *o*-toluidine. *m*-Aminoazotoluene,  $\text{Me}[3]\text{C}_6\text{H}_4[1]\text{N:N}[1']\text{C}_6\text{H}_3[2',4']\text{MeNH}_2$ , m.p.  $80^\circ$ . *m*-Nitrobenzene-azo-*p*-aminobenzene, m.p.  $213^\circ$  (*Meldola, Proc.* **1894**, 140). For condensation products of *p*-aminoazobenzene with aldehydes and ketones see *Reddelien, Ber.* **53**, 340.

**2,4-DIAMINOAZOBENZENE**,  $\text{PhN}_2\text{C}_6\text{H}_3(\text{NH}_2)_2$ , m.p.  $117^\circ$ , small yellow needles, is obtained from phenyl diazonium nitrate and *m*-phenylene diamine. Its hydrochloride is a commercial red dye known as *chrysoidine*. On reduction it breaks down into aniline and *as*-triaminobenzene,  $\text{C}_6\text{H}_3(\text{NH}_2)_3$  (p. 109).

*o*-Azoaniline, *sym-o,o'*-diaminoazobenzene,  $\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , copper-red flakes, m.p.  $134^\circ$ , is obtained by mild oxidation of *o*-phenylene diamine (p. 106), owing to the polymerisation of the *o*-quinone-diimine which is first formed (*Willstätter, Ber.* **38**, 2348). Its diacetyl compound, m.p.  $271^\circ$  is a reduction product of *o*-nitracetanilide (*Brand, Ber.* **39**, 4062).

*p*-Azoaniline, *sym-p,p'*-diaminoazobenzene,  $\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , has been obtained from nitracetanilide by reduction with zinc dust and alkali, from the diazo-compound of monoaceto-phenylene diamine and aniline, and also by reduction of *p,p'*-dinitroazobenzene (p. 137) (*Janovsky, Mo.* **6**, 455; *Witt, Ber.* **45**, 1134). It crystallises from alcohol in yellow needles, m.p.  $250\text{--}255^\circ$ .

The tetra-alkyl derivatives of *p,p'*-diaminoazobenzene are known as azylines. They were first obtained by the action of nitric oxide on dialkyl-anilines (*Lippmann, Ber.* **16**, 2768):  $2\text{Ph}\cdot\text{NR}_2 \rightarrow \text{R}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2$ . They are also formed by the interaction of the diazo-compound of dimethyl-*p*-phenylene diamine (p. 107) and tertiary aromatic amines (*Noelling, Ber.* **18**, 1143). The azylines are red basic dyestuffs; they dissolve in hydrochloric acid with a purple colour, and in acetic acid with an emerald-green colour. On reduction with  $\text{SnCl}_2$ , or  $\text{Sn}$  and  $\text{HCl}$ , they decompose into 2 mols. of dialkyl-*p*-phenylene diamine.

When heated at 100° with 4 mols. of an alkyl iodide, they are also broken down, tetra-alkyl-*p*-phenylene diamines being formed.

*m,m'*-Diaminoazobenzene, m.p. 155°, and tetramethyl-*m,m'*-diaminoazobenzene, m.p. 118°, are obtained from *m*-nitraniline and *m*-nitrodimethylaniline by reduction with zinc dust and alkali. In contrast to the *o*- and *p*-aminoazo-compounds, these compounds are only very weak dyes (*Binz*, Ber. 35, 4225).

3,2',4'-Triaminoazobenzene,  $\text{H}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3 \begin{matrix} \text{NH}_2 \\ \text{NH}_2 \end{matrix}$ , m.p. 144°, is best obtained from *m*-amino-phenylene-oxaminic acid,  $\text{NH}_2[1]\text{C}_6\text{H}_4[3]\text{NH} \cdot \text{CO} \cdot \text{COOH}$ , by diazotising, combining with *m*-phenylene diamine and hydrolysing. The action of sodium nitrite upon *m*-phenylene diamine hydrochloride gives rise to a mixture of bases, containing 3,2',4'-triaminoazobenzene, and mainly, phenylene-*bis*-azo-*m*-phenylene diamine,  $\text{C}_6\text{H}_4[\text{N}_2\text{C}_6\text{H}_3(\text{NH}_2)_2]_2$ , m.p. 116–118°, formed by singly and doubly diazotised *m*-phenylene diamine coupling with one and two mols. of unchanged base, respectively. The hydrochlorides of this mixture of bases form the commercial *phenylene brown*, *Bismarck brown*, *Vesuvine* or *Manchester brown*. It is used for dyeing cotton and leather (*Mohlau*, Ber. 30, 2203; *Eiermann*, Ber. 31, 188).

### (p) Hydrazine Derivatives

The simplest aromatic derivatives of hydrazine are: phenylhydrazine,  $\text{PhNH} \cdot \text{NH}_2$ , *as*-diphenylhydrazine,  $\text{Ph}_2\text{N} \cdot \text{NH}_2$ , and *sym*-diphenylhydrazine, or hydrazobenzene,  $\text{PhNH} \cdot \text{NHPh}$ .

Phenylhydrazine and *as*-diphenylhydrazine both contain a  $\text{NH}_2$ -group and resemble each other in many reactions, while *sym*-diphenylhydrazine behaves quite differently. *sym*-Diphenylhydrazine and its homologues, called "hydrazo-compounds" have been known the longest and will be dealt with first. They are closely related to the azo-compounds just discussed. The monophenyl- and *as*-phenylhydrazine groups will then be dealt with, and finally the triarylhydrazines, and tetra-aryl-hydrazines, which have been investigated chiefly by *Wieland*. The last two groups are related to the triarylhydrazyls, and diaryl-nitrogen compounds, which will be treated in the section on free radicals.

**HYDRAZO-COMPOUNDS.** *A. W. Hofmann* (1863) discovered *sym*-diphenylhydrazine when subjecting azobenzene to mild reduction, and called it hydrazobenzene because it differs from azobenzene in containing two more hydrogen atoms. This name has been universally adopted.

**Methods of formation.**—Azobenzene and related compounds are reduced to hydrazo-compounds by alcoholic ammonium sulphide, ethyl magnesium bromide, zinc dust and alcoholic potash, or sodium amalgam. U. S. Pat. 1,589,936 describes the catalytic reduction of azo- and azoxy-compounds to hydrazo-compounds. It is not necessary to isolate the azo-compounds, but azoxy-compounds can be treated directly with zinc dust and sodium hydroxide. For the electrolytic reduction of nitro-compounds to hydrazo-compounds in alkaline solution, see *Haüssermann*, Chem. Ztg., 17, 129, 209. *Bigiavi* (cf. *Atti Accad. Lincei* [6], 8, 167) has prepared hydrazo-benzene by oxidising aniline.

**Hydrazobenzene**, *sym*-diphenylhydrazine,  $\text{PhNH} \cdot \text{NHPh}$ , m.p. 131°, decomp. at a higher temperature, or when heated with alcohol at 120–130° (*Bishringer*, Ber. 36, 340), into azobenzene and aniline.



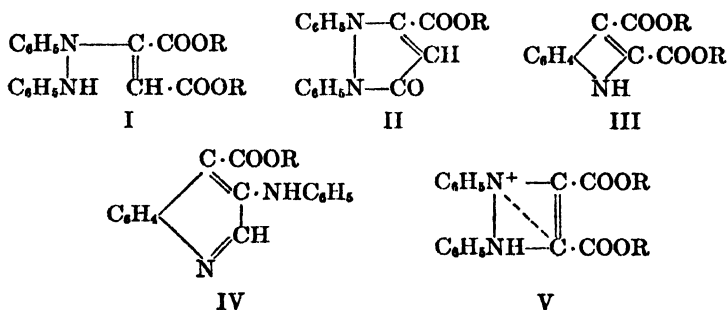
For the interpretation of this process see *Wieland*, Ber. 48, 1098; *Goldschmidt*, Ber. 55, 3217. It forms colourless flakes or plates, insoluble in water, readily soluble in alcohol and ether. It smells of camphor. It is oxidised in moist air to azobenzene, or in alcoholic solution, especially in the presence of alkali, with the formation of  $H_2O_2$ . It is a neutral substance and does not form salts with mineral acids, but under their influence it undergoes interesting internal rearrangements, the *benzidine* and *semidine* changes. Hydrazobenzene is decomposed by powerful reducing agents into two mols. of aniline. It reacts with nitrobenzene to give azobenzene and  $\beta$ -phenyl-hydroxylamine (*Bistrzycki*, Ber. 33, 476).

With phenyl isocyanate and phenyl mustard oil, hydrazobenzene gives substituted ureas (*Goldschmidt*, Ber. 23, 490; *Marckwald*, Ber. 25, 3113). It reacts with aldehydes in various ways. Formaldehyde gives  $CH_2(PhN \cdot N HPh)_2$  and

$CH_2 \begin{array}{c} \diagup NPh \cdot NPh \\ \diagdown NPh \cdot NPh \end{array} CH_2$ ; acetaldehyde gives  $MeCH \begin{array}{c} \diagup NPh \\ \diagdown NPh \end{array}$ ; benzaldehyde oxi-

dises it to azobenzene (*Rassow*, J. pr. 65, 97). With oxygen it oxidises so readily according to the reaction  $PhNHNHPh + O_2 = Ph \cdot NN \cdot Ph + H_2O_2$ , that very concentrated solutions of hydrogen peroxide may be prepared by this method (*Walton*, Am. 54, 3228). Mixed aliphatic-aromatic aldehydes combine with two mols. of hydrazobenzene to give colourless hydrazoins of the formula  $ArCH_2CH:(NPh \cdot NHPh)_2$ . When heated with  $CS_2$  it gives thiocarbanilide and sulphur. When heated with phthalic anhydride to  $200^\circ$  it gives  $N,N'$ -diphthalyl-benzidine,  $C_6H_4(CO)_2:N \cdot C_6H_4 \cdot C_6H_4:N:(CO)_2C_6H_4$  (*Simonyi*, Ber. 47, 2657). Certain nuclear-substituted hydrazobenzenes disproportionate when heated into azobenzene and aniline:  $Ph \cdot NH \cdot NH \cdot Ph = Ph \cdot N:N \cdot Ph + 2H$ ;  $Ph \cdot NH \cdot NH \cdot Ph + 2H = 2Ph \cdot NH_2$  (*Steglit*, Am. 38, 1736).

Hydrazobenzene and methyl acetylene-dicarboxylate (Vol. I, p. 578) unite to give a product to which *Diels* first assigned the formula I (Ann. 511, 168). Acids convert this substance into the *pyrazolone derivative* (II), and when boiled with xylene it loses aniline and becomes indole- $\alpha,\beta$ -dicarboxylic ester (III). When it is heated above its m.p. ( $151^\circ$ ), or boiled with pyridine or dimethylaniline, a *quinoline derivative* (IV) is formed. The fact that all these heterocyclic systems are formed makes it probable that the primary addition product has the polar formula V:



Monoacetyl-hydrazobenzene, m.p.  $159^\circ$ , decomposes at higher temperatures into azobenzene and acetanilide. Diacetyl-hydrazobenzene, m.p.  $105^\circ$  (*Stern*, Ber. 17, 379; *Schmidt*, Ann. 207, 327). For other acetyl derivatives, see *Biehinger*, Ber. 36, 137; *Bischoff*, Ber. 31, 3241; *Freundler*, C.r. 136, 1553.

*o*-, *m*-, and *p*-Methylhydrazobenzenes, or *sym-o*-, *m*-, *p*-tolylphenylhydrazines, m.p.  $101^\circ$ ,  $60^\circ$ ,  $87-88^\circ$ , are obtained from the benzene-azotoluenes (p. 138) by the action of zinc dust and alcohol and acetic acid (*Ritter*, Am. 52, 2815).

*sym*-Hydrazotoluenes,  $MeC_6H_4NH \cdot NHC_6H_4Me$ : *o*-, m.p.  $156^\circ$ , *m*-, liquid

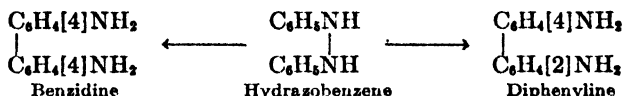
(Basilovsky, Ann. 207, 116), *p*-, m.p. 128°. **Hydrazoxylenes:** Noelling, Ber. 21, 3141.

*sym*-Dihalogeno-hydrazobenzenes have been obtained from the corresponding azo-compounds. *p*-Diamino-hydrazobenzene,  $\text{NH}_2[4]\text{C}_6\text{H}_4[1]\text{NH.NH}[1']\text{C}_6\text{H}_4[4']\text{NH}_2$ , m.p. 145° is obtained from *p*-dinitro-azobenzene by the action of ammonium sulphide (Janovsky, Ber. 18, 1136).

*as*-Nitrohydrazobenzenes have been obtained by reduction of nitroazo- and nitroazoxy-compounds, and also from chloro-dinitro- and chloro-trinitro-benzenes by the action of phenylhydrazine (E. Fischer, Ann. 190, 132; Willgerodt, J. pr. 37, 345; 44, 67; Werner, Ber. 32, 3280; Rassow, J. pr. 65, 97). *sym*-Hexanitro-hydrazobenzene, black crystals with a metallic lustre, m.p. 201°, is obtained from picryl chloride and hydrazine.

### The Benzidine and Semidine Rearrangements of Hydrazo-compounds

A remarkable rearrangement takes place when hydrazobenzene is treated with acids. When azobenzene is reduced in acid solution, the hydrazobenzene, which is presumably the first product, does not form salts, but is converted into *benzidine*, or *p,p'*-diamino-diphenyl, a diamine, in the presence of acids, even in the cold. Benzidine is a starting material in the manufacture of substantive cotton dyes, and is made industrially by the above method. In addition to benzidine, small quantities of *diphenylene* (p. 498) or *o,p*-diamino-diphenyl are formed (Bandrowski, Ber. 17, 1181):

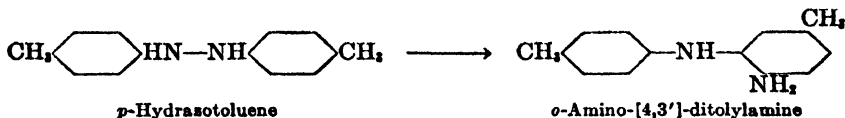


The main change, the migration of the two amino groups into the *p*-position to the point of union of the two rings is called the *benzidine rearrangement*. This change is an intramolecular process, for a mixture of 2,2'-dimethoxy-, and 2,2'-diethoxy-hydrazobenzene gives only 3,3'-dimethoxy- and 3,3'-diethoxy-benzidines, and no mixed methoxy-ethoxybenzidine (Chapman, J. 1933, 806).

The change is best effected by mineral acids, although boiling formic or acetic acid will also convert hydrazobenzene into acyl-compounds of benzidine (Sachs, Ber. 35, 1433).

*sym*-*o*- and *m*-Ditolyl-hydrazines or *o*- and *m*-hydrazotoluenes and other hydrazo-compounds in which the *p*-positions to the imino-groups in both rings are free give, with acids, *p*-diamino-ditolyls or *tolidines*, etc.

When, however, *p*-hydrazotoluene is treated with aqueous mineral acids, it changes partly into *p*-azotoluene and *p*-toluidine, and partly into *o*-amino-ditolylamine (Jacobson, Ber. 27, 2700). The latter is the chief product when  $\text{SnCl}_2$  and  $\text{HCl}$  are used:



This is called the *semidine transformation* because only one  $\text{NH}$ -group is changed into  $\text{NH}_2$ , and not both as in the benzidine rearrangement. In singly *p*-substituted hydrazobenzenes the amino-group may enter the *o*- or *p*-position to the imino-group; the rearrangement is then called an *o*- or *p*-semidine rearrangement.



When this is heated with conc. HCl, phenylhydrazine hydrochloride is formed.



If free sulphurous acid is used in the reduction of a diazonium salt in acid solution, either the so-called phenyl-benzene-sulphazide,  $\text{PhNHNHSO}_3\text{Ph}$  (p. 155), or azobenzene-*p*-hydrazine sulphonic acid,  $\text{PhN} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{SO}_3\text{H}$  (p. 155) is formed, according to the concentration of acid.

*p*-Nitrophenyl-diazonium nitrate and two mols. of potassium sulphite give *p*-nitrophenyl-hydrazine disulphonate,  $\text{C}_6\text{H}_4(\text{NO}_2)\text{N}(\text{SO}_3\text{K})\text{NH}(\text{SO}_3\text{K})$ , which is quantitatively decomposed to *p*-nitrophenyl-hydrazine by HCl. Similarly phenyl-hydrazine disulphonate,  $\text{PhN}(\text{SO}_3\text{K})\text{NH}(\text{SO}_3\text{K})$  is obtained from benzene diazo-sulphonate and  $\text{K}_2\text{SO}_3$ , or more conveniently from nitroso-acetanilide and  $\text{K}_2\text{SO}_3$  (p. 111); it is decomposed by hot HCl to phenylhydrazine and sulphuric acid, and to benzene diazosulphonate by alkali (*Bamberger*, Ber. 30, 374).

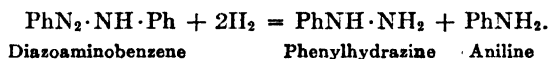
(b) Potassium diazobenzene-sulphonate is reduced with acetic acid and zinc dust.

(c) Diazonium chlorides are reduced with  $\text{SnCl}_2$  and HCl (*Meyer*, Ber. 16, 2976; *Fischer*, Ber. 17, 572), or electrochemically:

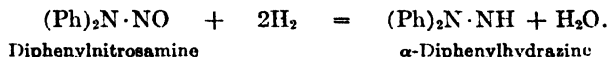


The alkali-metal salts of diazo- and isodiazobenzene (p. 120) and potassium isodiazobenzene-sulphonate are reduced to phenylhydrazine by sodium amalgam (*Hantzsch*, Ber. 30, 339).

2. Diazoamino-compounds, on reduction with zinc dust and acetic acid in alcoholic solution break down into anilines and hydrazines:



3. Reduction of nitrosamines (p. 110) with zinc dust and acetic acid gives *as*-alkyl-phenyl- or diphenyl-hydrazines (p. 148). A similar method of preparing aliphatic hydrazines has been referred to (Vol. I, p. 202):



*History.*—*Strecker* and *Römer* (1871) obtained potassium phenylhydrazine sulphonate,  $\text{PhNH} \cdot \text{NHSO}_3\text{K}$ , by treating phenyl diazonium nitrate with potassium bisulphite. On treating diazotised sulphanilic acid with the same reagent they obtained a soluble potassium salt, which, on boiling with hydrochloric acid gave a crystalline compound, phenylhydrazine-*p*-sulphonic acid,

$\text{C}_6\text{H}_4 \begin{matrix} \swarrow \text{NH} \cdot \text{NH}_2 [1] \\ \searrow \text{SO}_3\text{H} [4] \end{matrix}$ , the first primary aromatic hydrazine derivative to be prepared. *E. Fischer* (1875) succeeded in preparing phenylhydrazine hydrochloride by boiling potassium phenylhydrazine sulphonate with hydrochloric acid, and by treating the hydrochloride with caustic alkali he isolated the free phenylhydrazine, which is an exceedingly reactive compound (Ber. 8, 589).

*Properties.*—The aromatic hydrazines are monacid bases, sparingly soluble in water, but freely soluble in alcohol and ether. On boiling under ordinary pressure they undergo slight decomposition, but they boil unchanged under reduced pressure. They are readily oxidised

in air, assuming a brown colour (*Chattaway*, J. 91, 1323), and they reduce Fehling's solution.

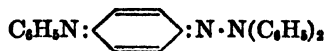
**Phenylhydrazine**,  $\text{PhNH} \cdot \text{NH}_2$ , forms vat crystals, m.p.  $19.6^\circ$ , b.p.  $241\text{--}242^\circ$  (760 mm.) with slight decomp., b.p. (12 mm.)  $120^\circ$ ,  $d_{20}^{21}$  1.091. As mentioned under the general methods of formation, it is prepared by reduction of phenyl diazonium chloride. Small quantities are formed when hydrazine hydrate is heated to  $220^\circ$  with phenol (*Hoffmann*, Ber. 31, 2909). Its reactions are described below. It is of industrial importance as one of the starting materials in the preparation of *antipyrine*. It has been used very largely as a reagent for aldehydes and ketones, and has played a very important part in the investigation of the carbohydrates. It is a poison, and in certain persons induces a skin disease.

**Phenylhydrazine hydrochloride**,  $\text{PhNH} \cdot \text{NH}_2 \cdot \text{HCl}$ , crystallises in lustrous white flakes, sparingly soluble in conc. hydrochloric acid. It gives *p*-phenylene diamine when heated with hydrogen chloride at  $200^\circ$ . Salts with carboxylic acids have been prepared (*de Vries*, Ber. 27, 1521). **Sodio-phenylhydrazine**, obtained by dissolving sodium in phenylhydrazine, is a brick-red amorphous mass, which reacts with alkyl and acyl halides giving phenylhydrazine derivatives (p. 150; *Michaelis*, Ber. 19, 2448; 22, R 664). **Potassio-phenylhydrazine**, see *Michaelis*, Ber. 20, 47.

**SUBSTITUTED PHENYLHYDRAZINES** (*Bischler*, Ber. 22, 2801, 2809; *Votocck*, Tchech. 1, 346; Bull. 35, 668). ***p*-Fluoro-phenylhydrazine**, m.p.  $39^\circ$ , is obtained by diazotising *p*-fluoro-aniline and reducing with sodium sulphite (*Schiemann*, Ber. 66, 727). ***p*-Chloro-phenylhydrazine**, m.p.  $83^\circ$ , ***p*-bromo-phenylhydrazine**, m.p.  $106^\circ$ , ***p*-iodo-phenylhydrazine**, m.p.  $103^\circ$ . **2,4,6-Trichloro-phenylhydrazine**, m.p.  $143\text{--}144^\circ$ , is prepared from trichloro-phenyl-diazonium chloride by the action of  $\text{SnCl}_2$ . Various compounds with aldehydes and ketones, see *Chattaway*, J. 1931, 1740. ***o*-Nitro-phenylhydrazine**, m.p.  $90^\circ$ , brick-red needles (*Klieeisen*, Ber. 27, 2549). ***o*-Nitro-*sym*-formyl-phenylhydrazide**, m.p.  $177^\circ$  (*Bischler*, Ber. 22, 2801). For the formation of heterocyclic compounds from these *o*-nitro-compounds, see p. 151. ***m*-Nitro-phenylhydrazine**, m.p.  $93^\circ$ , is prepared from *m*-nitraniline by method 1c (*van der Haar*, Weekblad 14, 147). ***p*-Nitro-phenylhydrazine**, m.p.  $157^\circ$  (decomp.) is very useful for isolating and characterising aldehydes and ketones. **2,4-Dinitro-phenylhydrazine**, yellow prisms, m.p.  $198^\circ$ , is obtained from dinitro-bromobenzene and hydrazine hydrate (*Curtius*, J. pr. 76, 369). **2,4,6-Trinitro-phenylhydrazine**, reddish-brown prisms, m.p.  $186^\circ$  (*Curtius*, J. pr. 50, 271). ***p*-Acetyl-amino-phenylhydrazine**,  $\text{CH}_3\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHNH}_2$ , m.p.  $110^\circ$ , is prepared by diazotising mono-acetyl-*p*-phenylene diamine and method 1c (*Franzen*, Ann. 412, 35).

**HOMOLOGOUS PHENYLHYDRAZINES**. ***o*-Tolylhydrazine**, m.p.  $59^\circ$ ; ***m*-tolylhydrazine**, liquid; ***p*-tolylhydrazine**, m.p.  $65^\circ$ . **Bromo-*o*- and -*p*-tolylhydrazines**, see *Chattaway*, J. 109, 582. ***p*-Xylhydrazine**, m.p.  $78^\circ$ . **Pseudo-cumylhydrazine** (*E. Fischer*, Ann. 212, 338; *Gallinek*, Ber. 18, 3175; *Willgerodt*, J. pr. 71, 398).

***as*-Diphenylhydrazine**,  $\text{Ph}_2\text{N} \cdot \text{NH}_2$ , m.p.  $44^\circ$ , b.p. (50 mm.)  $220^\circ$ , obtained from diphenylnitrosamine (p. 111) by reduction, forms difficultly soluble diphenylhydrazones with monosaccharoses. Ferric chloride and other acidic oxidising agents, such as  $\text{Br}$ ,  $\text{HOCl}$ ,  $\text{HOBr}$ , convert it into tetraphenyl-tetrazene and an intensely coloured mauve dye, the hydrochloride of quinone-anil-diphenylhydrazone, m.p.  $147^\circ$  (cf. p. 165):



(*Wieland*, Ber. 43, 3260). For supercooling phenomena and molecular configuration see *Vörlander*, Ber. 68, 2269. For melting and supercooling phenomena ("liquid crystals") see *Vörlander*, Ber. 68, 2269.

**Triphenylhydrazine**,  $\text{Ph}_2\text{N} \cdot \text{NHPh}$ , m.p.  $142^\circ$ , is produced by the action of  $\text{PhMgBr}$  on  $\beta$ -phenylhydroxylamine. Alcoholic  $\text{HCl}$  converts it into  $\text{N}$ -phenylbenzidine,  $\text{PhNH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$  (*Busch*, Ber. 40, 2099). Its conversion into free triphenyl-hydrazyl,  $\text{Ph}_2\text{N} \cdot \text{NPh}$ , is discussed in the section on free radicals.

**Tetraphenylhydrazine**,  $\text{Ph}_2\text{N} \cdot \text{NPh}_2$ , m.p.  $147^\circ$  (decomp.) is obtained from diphenylamine by oxidation with potassium permanganate or lead dioxide, and from sodio-diphenylamine  $\text{Ph}_2\text{N} \cdot \text{Na}$  by the action of iodine (*Wieland*, Ber. 39, 1501). It dissolves in conc. sulphuric acid with an intense blue colour, being partly converted into  $\text{N}, \text{N}'$ -diphenyl-benzidine,  $\text{PhNH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NHPh}$  (*Ushakov*, C. 1907, I, 406).  $\text{HCl}$  breaks it down into diphenylamine and  $p$ -chloro-anilino-triphenylamine (p. 108), diphenyl-chloramine,  $\text{Ph}_2\text{NCl}$  being probably formed as an intermediate product (*Gamburjan*, Ber. 41, 3508). For its thermal dissociation, see Vol. IV, and *Wieland*, Ann. 392, 156. ***p*-Nitro-tetraphenylhydrazine**, orange-red plates, m.p.  $145^\circ$ , has been obtained from the base by the action of amyl nitrite (*Wieland*, Ann. 392, 186).

**Tetra-*p*-tolylhydrazine**,  $(\text{MeC}_6\text{H}_4)_2\text{N} \cdot \text{N}(\text{C}_6\text{H}_4\text{Me})_2$ , m.p.  $136^\circ$ , is obtained from *p*-ditolylamine on oxidation with  $\text{KMnO}_4$ , and from tetra-*p*-tolyl-tetrazene (p. 165) on heating. It combines with acids, halogens, non-metallic and metallic chlorides, such as  $\text{PCl}_5$ ,  $\text{SbCl}_5$ ,  $\text{SnCl}_4$ , etc., forming salt-like addition products, dark violet in colour, from which the unchanged hydrazine is regenerated by the addition of water. These addition products are rather unstable, and in inert solvents soon dissociate into *p*-ditolylamine and derivatives of ditolyl-hydroxylamine,  $(\text{MeC}_6\text{H}_4)_2\text{NOH}$ . The latter immediately undergo a further change into derivatives of ditertiary dihydrophenazine (*Wieland*, Ber. 41, 3478).

**Tetra-*p*-anisyl-hydrazine**, m.p.  $90.5^\circ$ , partially dissociates in benzene solution into dianisyl-nitrogen, even in the cold (*Wieland*, Ber. 45, 2600). See Vol. IV.

**Reactions of the phenylhydrazines.**—1. The phenylhydrazines are not easily reduced. On mild oxidation (e.g., by  $\text{HgO}$  acting on their sulphates or sulphonates), they are converted into diazonium salts. On boiling with  $\text{CuSO}_4$ ,  $\text{FeCl}_3$ ,  $\text{K}_2\text{CrO}_4$ , Caro's acid, or  $\text{NaOCl}$  (*Chattaway*, J. 95, 1065), they lose  $\text{N}_2$  and the corresponding benzene hydrocarbons are formed. This reaction can be used for replacing the diazonium group by hydrogen, or by halogen if instead of the free phenylhydrazine its hydrochloride, hydrobromide, or hydriodide is used (*Zincke*, Ber. 18, 786; *Gattermann*, Ber. 25, 1074; *Cain*, Proc. 24, 76). The phenylhydrazines can be quantitatively determined by estimating the nitrogen evolved. They reduce Fehling's solution (*Strache*, Ber. 26, R 234). For other reducing actions of phenylhydrazine see *Walther*, Ber. 28, R 996; 29, R 977.

2. Sodium forms  $\alpha$ -sodio-phenylhydrazines (see above), hydrogen being evolved.

3. Nitrous acid forms nitroso-hydrazines (p. 164).

4. Alkyl halides replace the imino- and amino-hydrogen and finally give phenyl-hydrazonium compounds.

5. Acid radicals are also readily introduced into the phenylhydrazines.

6. Chlorine and bromine, if the temperature is kept low, convert the phenylhydrazines into the corresponding diazonium salts (p. 112). At higher temperatures and in the presence of mineral acids, nuclear-substituted halogeno-phenylhydrazines are formed (*Chattaway*, J. 93, 852; 95, 1065).

7. The phenylhydrazines combine with aldehydes and ketones to give compounds, which, as a rule, immediately lose water to form **phenylhydrazones** (p. 151). This reaction is characteristic for aldehydes and ketones.

8. When heated at  $200^{\circ}$  with fuming hydrochloric acid, the phenylhydrazines are converted into *p*-phenylene diamines (*Thiele*, Ber. 28, 1538).

9. When phenylhydrazine is heated with cuprous chloride, cuprous bromide, or copper powder, it decomposes into aniline, nitrogen, and ammonia (*Arbusov*, J. Russ. Phys. Chem. Soc. 45, 69).

10. When nitroso-anilines act upon phenylhydrazines both oxidation to azoxy- and azo-compounds, and condensation occur, the latter giving rise to diazobenzene-nitroso-anilines (diazamino-hydroxybenzenes),  $\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\text{N}(\text{OH})\cdot\text{N}:\text{NPh}$  (or a tautomeric formula) (*Fischer*, J. pr. 92, 60).

11. With chloroformic ester in pyridine, hydrazo-esters of the type  $\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{COOR}$  are formed almost quantitatively. When these are oxidised with permanganate they are converted into azo-esters,  $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{COOR}$ , and on further oxidation, azoxy-esters,  $\text{Ph}\cdot\text{N}(\text{O})\cdot\text{N}\cdot\text{COOR}$ , are formed (*Pieroni*, Gazz. 54, 162).

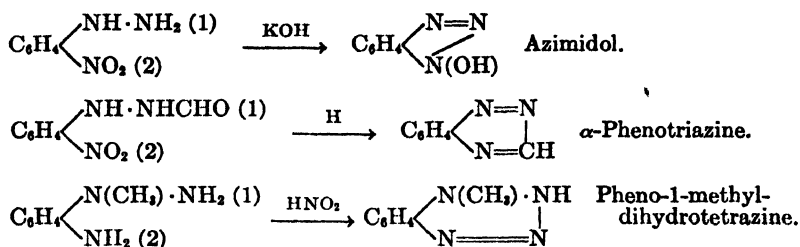
12. With aliphatic or aromatic isocyanates, the phenylhydrazines form 1,4-substituted semicarbazides,  $\text{ArNHNH}\cdot\text{CONHR}$  (*Pacilly*, Rec. 55, 101).

**PHENYL-ALKYL-HYDRAZINES.** The asymmetrical compounds which contain one alkyl residue are called  $\alpha$ -compounds, and the symmetrical ones,  $\beta$ -compounds.

*Methods of formation.*—1. Both isomers are formed by the action of alkyl bromides on phenylhydrazine (*Fischer*, Ber. 17, 2844; Ann. 199, 325). The  $\beta$ -compounds are isolated by making use of the fact that when oxidised with mercuric oxide they form azo-compounds which are volatile, and are unattacked by acids, and can be easily separated from the other products. They are reconverted into the original  $\beta$ -alkyl-phenylhydrazine on reduction. The  $\alpha$ -compounds are formed: 2. By the action of alkyl bromides on sodio-phenylhydrazine (*Michaelis*, Ber. 19, 2450; Ber. 22, R 664). 3. By the reduction of the corresponding nitrosamines (p. 110) with zinc dust, and 4. by treating  $\beta$ -aceto-phenylhydrazine,  $\text{PhNH}\cdot\text{NHCOCH}_3$  with alkyl halides, followed by hydrolysis by boiling with acids (*Widman*, Ber. 26, 946).

$\alpha$ -Methyl-phenylhydrazine,  $\text{PhNMe}\cdot\text{NH}_2$ , b.p.  $131^{\circ}$  (35 mm.), rearranges to methyl-*p*-phenylene diamine.  $\alpha$ -Ethyl-phenylhydrazine,  $\text{PhNEt}\cdot\text{NH}_2$ , b.p.  $237^{\circ}$ . Both are oxidised to tetrazenes (p. 165).  $\alpha$ -Ethyl-phenylhydrazine and ethyl bromide combine to give diethyl-phenylhydrazonium bromide,  $\text{PhNEt}_2\text{Br}\cdot\text{NH}_2$ , which gives diethylanilines on reduction. With methyl iodide, phenyl-methyl-ethyl-hydrazonium iodide,  $\text{PhNMeEtI}\cdot\text{NH}_2$ , m.p.  $119^{\circ}$  is formed, which can be resolved by means of its *d*-camphor- $\beta$ -sulphonate into a laevorotatory base with an asymmetrical nitrogen atom (*Singh*, J. 103, 604).  $\alpha$ -Propyl,  $\alpha$ -isopropyl,  $\alpha$ -isobutyl-,  $\alpha$ -isoamyl-phenylhydrazine, boil at  $247^{\circ}$ ,  $236^{\circ}$ ,  $240\text{--}245^{\circ}$ ,  $262^{\circ}$  (*Michaelis*, Ber. 30, 2809).  $\alpha$ -*d*-Amylphenylhydrazine,  $\text{CH}_3(\text{C}_2\text{H}_5)_4\text{CH}\cdot\text{CH}_2\text{N}(\text{C}_6\text{H}_5)\cdot\text{NH}_2$ , b.p.  $173\text{--}175^{\circ}$  (50 mm.), has been used for the direct resolution of racemic aldehydes and ketones (*Neuberg*, Ber. 38, 868). Ethylene-phenylhydrazine,  $\text{C}_6\text{H}_5\text{N}(\text{NH}_2)\text{C}_2\text{H}_4\cdot\text{N}(\text{NH}_2)\text{Ph}$ , m.p.  $90^{\circ}$  (*Michaelis*, Ber. 21, 3203; *Hischmann*, Ann. 310, 156). *as-o*-Aminophenylmethylhydrazine,  $\text{NH}_2[2]\text{-C}_6\text{H}_4[1]\text{N}(\text{Me})\text{NH}_2$ , an easily resinified oil, is produced from nitro-nitroso-methylaniline by reduction with alcoholic ammonium sulphide.

*Formation of heterocyclic compounds from o-substituted phenylhydrazines.*—When boiled with caustic potash, *o*-nitrophenylhydrazine is converted into azimidol (Vol. IV). The formyl-compound of *o*-nitrophenylhydrazine gives  $\alpha$ -phenotriazine when reduced with sodium amalgam and acetic acid. *as-o*-Aminophenylmethylhydrazine gives phenomethyl-dihydrotetrazine (Vol. IV) with nitrous acid:

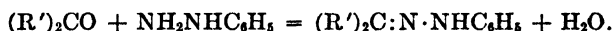


$\beta$ -Methyl and  $\beta$ -ethyl-phenylhydrazine are colourless oils, which oxidise in the air to benzene-azo-methane and -ethane (p. 138), and can be reobtained from these by reduction. The  $\beta$ -methyl-compound is also produced by boiling *antipyrine* with alcoholic potash (Knorr, Ber. 39, 3265).  $\beta$ -Allyl-phenylhydrazine, b.p. (110 mm.) 177° (Michaëlis, Ber. 22, 2233).

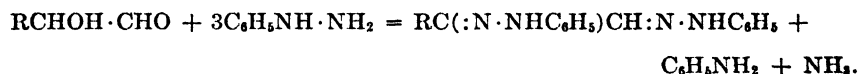
Di- and tri-alkylated phenylhydrazines are prepared from *sodio- $\alpha$ -methyl-phenyl-formyl-phenylhydrazine*,  $\text{PhNMe} \cdot \text{NNa} \cdot \text{CHO}$ , by the action of alkyl iodides, the formyl group being subsequently removed by means of conc.  $\text{HCl}$ . With alkyl iodides, dialkyl-phenylhydrazines give quaternary *azonium-compounds*, e.g.,  $\text{PhNMe} \cdot \text{I} \cdot \text{NH} \cdot \text{Me}$ , together with trialkyl-phenylhydrazines.  $\alpha, \beta$ -Dimethyl-phenylhydrazine,  $\text{PhNMe} \cdot \text{NHMe}$ , b.p. (7 mm.) 93°, and  $\alpha, \beta$ -diethyl-phenylhydrazine,  $\text{PhNEt} \cdot \text{NHEt}$ , b.p. (11 mm.) 111–115° are formed by the action of zinc dimethyl and zinc diethyl on benzene diazonium chloride (Bamberger, Ber. 35, 4179). Trimethyl-phenylhydrazine, b.p. (8 mm.) 93° (Harries, Ber. 27, 696).

### Phenylhydrazones and Osazones

Aldehydes and ketones form *phenylhydrazones* with phenylhydrazine. Phenylhydrazones are classified into *aldehydrazones* (Japp, Ann. 247, 194) if derived from aldehydes, and *kethydrazones*, if derived from ketones. The dihydrazones of  $\alpha$ -dicarbonyl compounds are known as *osazones* (Fischer, Ber. 21, 984; 41, 73):



$\alpha$ -Hydroxyaldehydes and  $\alpha$ -hydroxyketones also give osazones. A hydrazone is first formed, and then the excess of phenylhydrazine oxidises the alcoholic group next to the aldehydo- or keto-group, and converts it into carbonyl.



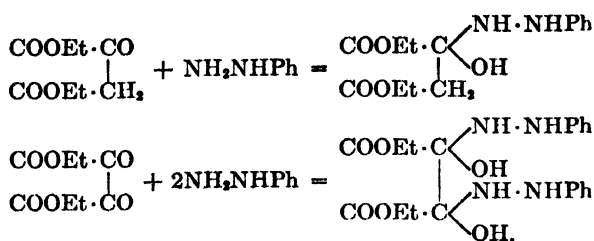
The formation of osazones has played an important part in the elucidation of the structure of the sugars.

Many phenylhydrazones of aldehydes and ketones are known in several isomeric forms, which are regarded as *cis-trans* isomers, by analogy with the better known isomerism of the oximes (see benzaldoxime, p. 273). The first instance of isomerism of osazones was discovered in 1895, when it was found that in the action of phenylhydrazine on diketosuccinic ester (Vol. I, p. 663) three isomers were formed (*cf.* benzil dioxime) (Anschütz, Ber. 28, 64). No reliable criterion for the configuration has yet been found.

The monoximes of  $\alpha$ -aldehydo-ketones and  $\alpha$ -diketones give *hydrazoximes* with phenylhydrazine, e.g., methyl-glyoxime gives methyl-glyoxalo-phenylhydrazoxime,  $\text{MeC}(:\text{NNHPh})\text{CH} : \text{NOH}$  m.p. 134° (Jonas, Ann. 262, 278).

In the formation of phenylhydrazones an addition product is probably first formed, corresponding, in constitution, to aldehyde-ammonia. In some cases such products have been isolated, e.g., those of oxalacetic ester and diketo-succinic ester. They readily lose water and become phenylhydrazones:

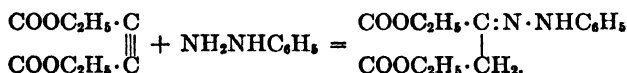




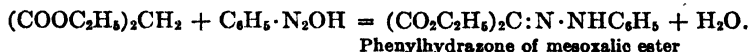
In the case of oxalacetic ester an ammonium salt of the formula  $\text{COOEt} \cdot \text{CH} : \text{C} \cdot (\text{ONH} \cdot \text{NPh}) \text{COOEt}$  might also be formed, but the fact that an addition product is formed by diketo-succinic ester is evidence in favour of the above mechanism. Phenyl-hydrazino-*p*-sulphonic acid (p. 180) seems to form only products of the formula  $\text{RCH}(\text{OH})\text{NHNHC}_6\text{H}_4\text{SO}_3\text{H}$  with aldehydes (*Blitz*, Ber. 35, 2000).

Phenylhydrazones were frequently referred to in Vol. I, before their systematic treatment, as they are used to characterise aliphatic aldehydes and ketones. They will be met with again in connection with aromatic compounds containing carbonyl groups. The following classes of aliphatic phenylhydrazones are mentioned under the heading of their parent compounds in Vol. I: phenylhydrazones of the simple aldehydes, simple ketones, diketones, glyoxalic acid, pyrotartaric acid, acetoacetic ester, laevulic acid, mesoxalic aldehyde, acetone-oxalic ester, mesoxalic acid, oxalacetic ester, acetone-dicarboxylic ester, acetone-diacetic acid, tetroses, oxalyl-diacetone, diketo-succinic acid, oxalo-succinic ester, arabinose, rhamnose, the glucoses, lactose, maltose, and isomaltose.

**Methods of formation of the phenylhydrazones.**—1. By the action of phenylhydrazine, *as*-alkyl-phenylhydrazines, or *as*-diphenylhydrazines on aldehydes and ketones (see above). 2. By the addition of phenylhydrazine to triply linked C atoms; thus the phenylhydrazone of oxalacetic ester may be obtained by the addition of phenylhydrazine to acetylene-dicarboxylic ester.



3. By the action of phenyl diazonium compounds on aliphatic compounds containing readily replaceable hydrogen atoms, such as malonic ester and acetoacetic ester (see p. 125).

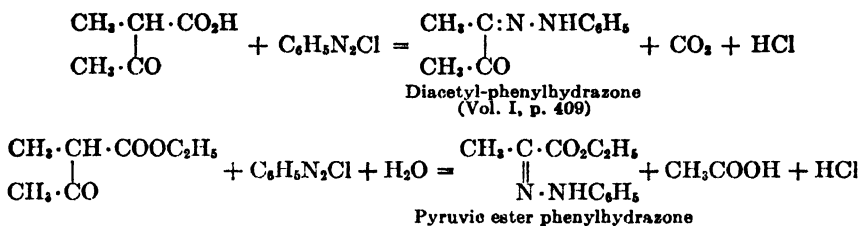


Some desmotropic compounds, such as mesityl-oxide oxalic ester (Vol. I, p. 603) and diaceto-succinic ester, in which the keto- and enol- (double enol) forms can be isolated, have been found to react with diazonium salts only in the enol form. Hence it seems that in all cases the azo-group first attacks the enol-hydroxyl, O-azo-compounds being formed, which spontaneously rearrange to C-azo-compounds, and finally to phenylhydrazones (*Dimroth*, Ber. 41, 4012). In some cases (see tribenzoyl-methane) the isolation of the intermediate compounds has been accomplished.

The compound obtained from malonic ester and phenyl diazonium hydroxide, and that obtained from mesoxalic ester and phenylhydrazine are identical. The compound formed from acetoacetic ester and phenyl diazonium salts is possibly tautomeric, possessing the hydrazone formula  $\text{PhNHN} : \text{C}(\text{OCCH}_3)_2\text{CO}_2\text{C}_2\text{H}_5$ , and also the formula of a benzene-azo-acetoacetic ester,  $\text{PhN} : \text{N} \cdot \text{CH}(\text{COCH}_3) \cdot \text{COOC}_2\text{H}_5$ , or that of the corresponding enol, because the ester dissolves in dilute sodium hydroxide to give a salt and separates again unchanged when carbon dioxide is passed through. This is best explained by assuming that an enolic com-

pound is present (*Bülow*, Ber. 32, 197; Ann. 312, 128). On the other hand, benzene-azo-acetoacetic ester can be converted by hydrolysis and removal of carbon dioxide into the hydrazone of pyruvic aldehyde,  $\text{PhNH}\cdot\text{N}:\text{CHCOCH}_3$ . The product obtained from cyanacetic ester and phenyldiazonium salts occurs in two forms:  $\alpha$ -, m.p.  $125^\circ$ , and  $\beta$ -, m.p.  $85^\circ$ , which are regarded as stereoisomeric hydrazones,  $\text{PhNH}\cdot\text{N}:\text{C}(\text{CN})\text{CO}_2\text{R}$ . In the presence of alkali the  $\beta$ -form readily rearranges to the  $\alpha$ -form (*Hantzsch*, Ber. 40, 4928). Glutaconic ester (Vol. I, p. 575) reacts with 2 mols. of phenyldiazonium salts with the formation of compounds containing both the phenylhydrazone and azo-groups:  $\text{CO}_2\text{R}\cdot\text{C}(\text{NNHPh})\text{CH}:\text{C}(\text{N}:\text{NPh})\cdot\text{CO}_2\text{R}$  (*Henrich*, Ber. 40, 4928). For the constitution of the products formed in the reactions of phenyldiazonium salts with aminocrotonic, methylaminocrotonic, and diethylaminocrotonic esters see *Prager*, Ber. 36, 1449.

The readiness with which phenylhydrazones are formed is so great that alkyl-acetoacetic acids and diazonium chlorides form phenylhydrazones of  $\alpha$ -diketones with liberation of  $\text{CO}_2$ , and alkyl-acetoacetic esters are converted into phenylhydrazones of  $\alpha$ -ketocarboxylic esters with elimination of the acetyl group:



Glyoxylic phenylhydrazone has also been prepared from malonic acid and phenyl diazonium chloride,  $\text{CO}_2$  being split off (*Busch*, J. pr. 71, 366). For the rules governing the elimination of acyl groups from diacyl-acetic esters by diazonium salts, see *Bülow*, Ber. 35, 915. The latter act like nitrous acid, which produces oximes under similar conditions (Vol. I, p. 465).

*Reactions of phenylhydrazones.*—On heating with dilute mineral acids, the phenylhydrazones decompose into their parent compounds. On heating in hydrogen the aldehyde-phenylhydrazones decompose into aniline and nitriles (*Ciusa*, Gaz. 51, II, 152). A number of phenylhydrazones have been converted, by careful reduction, into phenyl-hydrazino-compounds (cf. benzyl-phenylhydrazine, phenylhydrazino-acetic acid, p. 156) (*Bamberger*, Mo. 19, 427; *Harries*, Ber. 28, 1223). For their oxidation see *Freer*, Ber. 30, 736. Some add on hydrogen cyanide even more readily than the aldehydes and ketones themselves, forming cyano-hydrins or nitriles of  $\alpha$ -phenylhydrazido-carboxylic acids,  $\text{RCH}(\text{NHNHPh})\text{CN}$ ; see *Eilmer*, Ber. 33, 3550, *et al.*

There are few classes of compounds which form heterocyclic compounds so readily as the derivatives of hydrazine, and their intramolecular condensations have played a great part in the development of the chemistry of nitrogen-containing ring systems. Some of the most important condensations have already been discussed in the sections dealing with the phenylhydrazones of aliphatic compounds. These are listed below, whilst others will be mentioned in connection with the acid hydrazides.

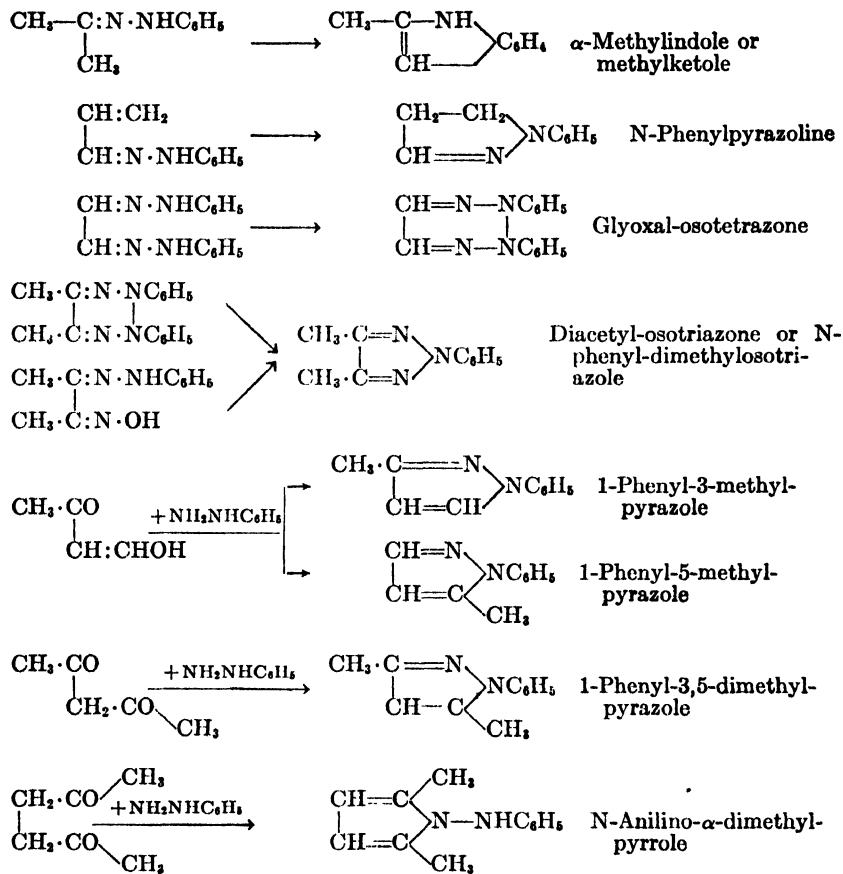
1. The phenylhydrazones of aldehydes, ketones, and ketonic acids give *indoles* on heating with  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$ , or mineral acids.
2. The phenylhydrazones of  $\alpha$ -olefine-aldehydes and -ketones rearrange to *pyrazolines*.
3. The osazones or *bis*-phenylhydrazones of  $\alpha$ -dialdehydes,  $\alpha$ -aldehydo-ketones, and  $\alpha$ -diketones give *osotetrazones* on oxidation.
4. The  $\alpha$ -osazones and *osotetrazones* give *osotriazoles* when boiled with acids.
5. The  $\alpha$ -hydrazoximes give *osotriazoles* on treatment with dehydrating agents.

6. The phenylhydrazones of 1,3-hydroxymethylene-ketones and  $\beta$ -diketones, readily lose water and form *pyrazoles* which are nitrogen derivatives of 1,3-cyclohexenones.

7. The phenylhydrazones of 1,4-diketones condense to *N-anilido-pyrroles*.

These cyclic condensation products can often be obtained directly from the starting materials without isolating the hydrazones themselves.

The types of heterocyclic compounds obtainable from the phenylhydrazones are given below (see also Vol. IV):



### Phenylhydrazine Derivatives of Inorganic Acids

Thionyl-phenylhydrazine,  $\text{PhNH} \cdot \text{N} : \text{SO}$ , m.p.  $105^\circ$ , forms sulphur-yellow prisms. It is obtained by a similar method to the thionyl-alkylamines (Vol. I, p. 200) and thionyl-anilines (p. 86) by the action of thionyl chloride on phenylhydrazine. Any phenylhydrazine with a free amino-group gives a thionyl-phenylhydrazine with thionyl chloride (*Klieeisen*, Ber. 27, 2549). Thionyl-phenylhydrazine is also obtained smoothly from thionyl-aniline and phenylhydrazine. Phenylhydrazine-sulphinic acid,  $\text{PhNH} \cdot \text{NH} \cdot \text{SOOH}$ , obtained by the action of phenylhydrazine on sulphur dioxide, gives thionyl-phenylhydrazine on gentle heating (*Michaelis*, Ber. 23, 474). With thionyl chloride, acetyl chloride, and other acid chlorides, thionyl-phenylhydrazine forms phenyl diazonium

chloride (*Michaelis*, Ann. 270, 114). The formula  $\text{Ph} \cdot \text{NH} \cdot \text{N} : \text{SO}$  agrees with the absorption spectrum, whilst  $\text{Ph} \cdot \text{N} : \text{N} \cdot \text{SOH}$  and  $\text{Ph} \cdot \text{N} - \text{NH}$  do not (*Hutchinson*, Ber. 47, 514).

**Phenylhydrazino-sulphonic acid**,  $\text{PhNH} \cdot \text{NHSO}_3\text{H}$ . The potassium salt of this acid is formed by the reduction of potassium benzene diazosulphonate with sulphur dioxide, or alkali bisulphite. For the action of mineral acids on this salt, and for the part played by it in the discovery of phenylhydrazine, see p. 147.

**p-Nitro-phenylhydrazine-disulphonic acid**,  $\text{C}_6\text{H}_4(\text{NO}_2)\text{N}(\text{SO}_3\text{H})\text{NH}(\text{SO}_3\text{H})$ . The dipotassium salt of this acid crystallises in minute yellow needles, and is obtained from nitro-diazobenzenic ester, nitrodiazobenzene nitrate, or potassium nitrophenyl-*iso*-diazotate by the action of excess of a solution of sulphite. Hydrochloric acid decomposes it giving *p*-nitro-phenylhydrazine. It dissolves in excess of caustic potash to form a red tri-potassium salt,  $\text{C}_6\text{H}_4(\text{NO}_2)\text{N}(\text{SO}_3\text{K})\text{NK}(\text{SO}_3\text{K})$  (*Bamberger*, Ber. 29, 1830).

**Azobenzene-*p*-hydrazine-sulphonic acid**,  $\text{PhN} : \text{N} \cdot \text{C}_6\text{H}_4\text{NH} \cdot \text{NHSO}_3\text{H}$ , forms bluish-red needles, decomposing below  $100^\circ$ . It is obtained by the action of  $\text{SO}_2$  on a concentrated solution of phenyldiazonium sulphate (p. 147). It condenses with aldehydes with loss of the sulphonic group (*Tröger*, J. pr. 78, 369).

**Phenyl benzene-sulphazide**,  $\text{PhNH} \cdot \text{NH} \cdot \text{SO}_2\text{Ph}$ , m.p.  $148-150^\circ$  (decomp.) is obtained from phenylhydrazine and benzene sulphonyl chloride in ether solution, and from aqueous diazonium salts by the action of  $\text{SO}_2$  (p. 147) or sodium hydrosulphite (*Grandmougin*, Ber. 40, 422).

For the action of  $\text{PCl}_3$ ,  $\text{POCl}_3$ ,  $\text{PSCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{BCl}_3$ , and  $\text{SiCl}_4$  on phenylhydrazine see *Michaelis*, Ann. 270, 123.

### Carboxylic Derivatives of Phenylhydrazine

Carboxylic residues of the most varied character can be introduced into phenylhydrazine as readily, and usually by the same methods, as into aniline.

The acid hydrazides and the hydrazino-acids are able to form heterocyclic compounds in the same way as the phenylhydrazones themselves. After each group of carboxylic phenylhydrazine derivatives the chief reactions by which heterocyclic compounds are produced will be summarised.

The *nitrohydrazones*, *amidrazones*, and *formazyl* compounds will be dealt with after the simple carboxylic derivatives of phenylhydrazine.

**DERIVATIVES OF FATTY ACIDS.** The fatty acid residues readily enter the amino-group of phenylhydrazine, *sym*- or *β*-acyl compounds being formed (*Jarosky*, Mo. 31, 951). The asymmetrical *α*-acyl-compounds are prepared by treating: (1) sodiophenylhydrazine with acid chlorides or anhydrides (*Michaelis*, Ber. 22, R 664); (2) *β*-aceto-phenylhydrazine with acid halides and then boiling with dilute sulphuric acid, which removes the *β*-aceto-group but does not affect that in the *α*-position (*Widman*, Ber. 26, 945); (3) a cold benzene solution of *N*-chloro-acetanilide,  $\text{COCH}_3 \cdot \text{NCl} \cdot \text{Ph}$ , with finely divided  $\text{NaNH}_2$  (*Short*, J. 119, 1445).

The *as*- and the *sym*-phenylhydrazides can be distinguished by their reaction with ferric chloride and conc.  $\text{H}_2\text{SO}_4$  (*Bilow's* reaction). The *sym*-compounds give reddish to bluish-violet colours, whilst the *as*-compounds remain colourless.

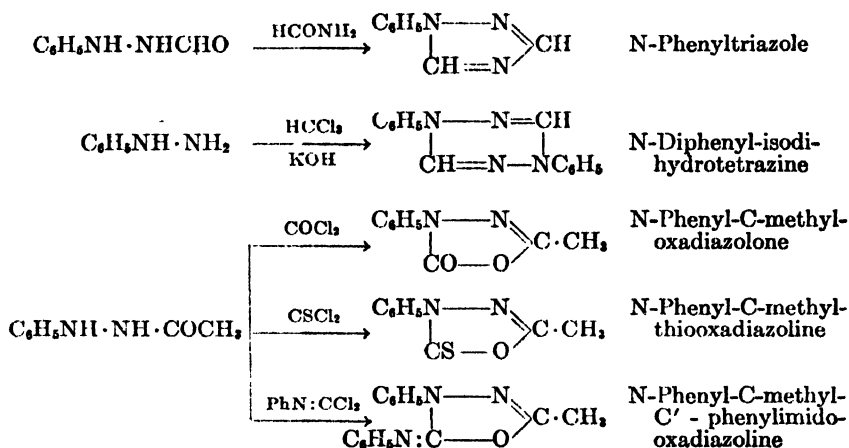
***sym*-Formyl-phenyl hydrazide**,  $\text{PhNH} \cdot \text{NH} \cdot \text{CHO}$ , m.p.  $145^\circ$ , is obtained from formic acid or ethyl formate with phenylhydrazine (*de Vries*, Ber. 27, 1522; *Baidakovsky*, C. 1903, I, 829).

***as*- or *α*-Aceto-phenylhydrazide**,  $\text{PhN}(\text{COCH}_3)\text{NH}_2$ , m.p.  $124^\circ$ ; is obtained from *α,β*-diaceto-phenylhydrazide on heating with dilute sulphuric acid (*Widmann*, Ber. 27, 2965). ***sym*- or *β*-Acetophenylhydrazide**,  $\text{PhNH} \cdot \text{NHCOCH}_3$ , m.p.  $128^\circ$ , is obtained from phenylhydrazine by the action of acetic anhydride or on boiling with acetic acid (*E. Fischer*, Ann. 190, 129). ***α,β*-Diaceto-phenylhydrazide**,  $\text{PhN}(\text{COCH}_3)\text{NH}(\text{COCH}_3)$ , m.p.  $106^\circ$ , from potassio-phenylhydrazide in ether with acetyl chloride (*Michaelis*, Ber. 20, 47). **Propionyl- and isobutyryl-**

phenyl-hydrazides, m.p. 158° and 143° (Leighton, Am. Ch. J. 20, 676). For phenylhydrazides of higher fatty acids see Brannas, Am. 42, 1478).

**Formation of heterocyclic compounds from hydrazides of fatty acids.**—When *sym*-formylphenylhydrazide is heated with formamide, *N*-phenyltriazole (Vol. IV) is formed (Pellizzari, Gazz. 24, II, 222). Another formyl derivative, *N*-phenyl-*iso*-*dihydro*-tetrazine, is produced by the action of chloroform and caustic alkali on phenylhydrazine, whereas primary amines when treated in this way yield carbylamines or isonitriles.

The *sym*- or  $\beta$ -acyl-phenyl-hydrazides react with phosgene, thiophosgene, or isocyno-phenyl chloride forming *oxadiazoline* derivatives (Freund, Ber. 26, 2870). These are heterocyclic compounds which may also be regarded as cyclic derivatives of carbonic acid.

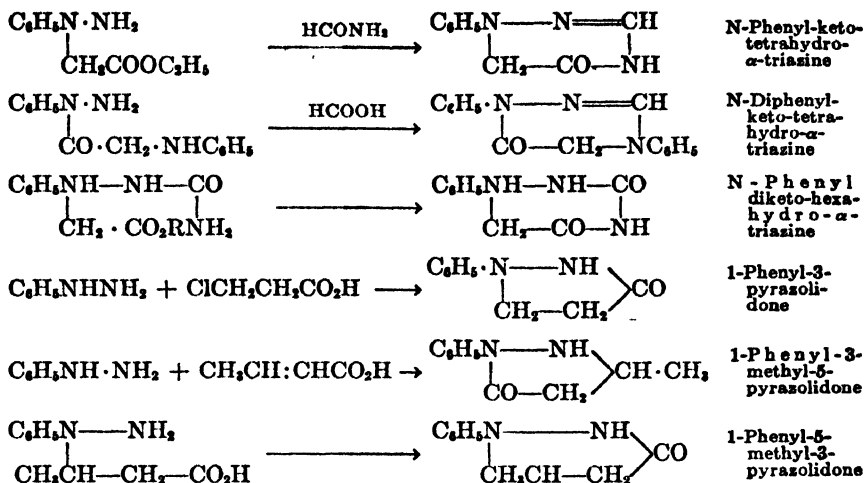


**THE HYDROXY-ACID DERIVATIVES OF PHENYLHYDRAZINE.** *sym*-Phenylhydrazino-acetic acid,  $\text{PhNH}\cdot\text{NH}\cdot\text{CH}_2\text{COOH}$ , m.p. 158°, is obtained by the reduction of glyoxylic acid phenylhydrazone, into which it is reconverted on oxidation with ammoniacal copper solution. Its ester, together with the asymmetrical compound, is formed from phenylhydrazine with chloroacetic ester, whereas with chloroacetic acid or its amides, *as*-phenylhydrazino-acetic acid,  $\text{PhN}(\text{NH}_2)\text{CH}_2\text{COOH}$ , m.p. 167°, or its derivatives, are obtained (Busch, Ber. 36, 3877). For the reactions of chloroacetyl ureas and urethanes with phenylhydrazine see Frerichs, Arch. Pharm. 237, 331, 346. The *as*-ester is obtained by the reduction of nitrosophenyl-glycine ester,  $\text{PhN}(\text{NO})\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$  (Harries, Ber. 28, 1224); amide, m.p. 150°; anilide, m.p. 149°; *as*-phenylhydrazide,  $\text{PhN}(\text{NH}_2)\text{CH}_2\text{CON}(\text{NH}_2)\text{Ph}$ , m.p. 155° (Rupe, Ann. 301, 55); *sym*-phenylhydrazide,  $\text{PhN}(\text{NH}_2)\text{CH}_2\text{CONHNHPh}$ , m.p. 178° (Rupe, Ber. 29, 622).

*as*-Phenylhydrazino- $\beta$ -propionic ester,  $\text{PhN}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{COC}_2\text{H}_5$ , b.p. 175° (9 mm.) is obtained from nitroso- $\beta$ -anilino-propionic ester (Harries, Ber. 29, 515). *as*-Phenylhydrazino- $\beta$ -butyric acid,  $\text{PhN}(\text{NH}_2)\text{CHCH}_2\text{CH}_2\text{COOH}$ , m.p. 111°, is obtained from  $\beta$ -chlorobutyric acid by the action of phenylhydrazine (Werner, J. pr. 45, 76).

**Formation of heterocyclic compounds from phenylhydrazino acids.**—1. *as*-Phenylhydrazino-acetic ester condenses with formamide to give *phenyl-keto-tetrahydro- $\alpha$ -triazine*. 2. Similarly, *as*-anilino-acetic  $\alpha$ -phenylhydrazide,  $\text{PhN}(\text{NH}_2)\text{COCH}_2\text{NHPh}$ , gives *N*-diphenyl-ketotetrahydro- $\alpha$ -triazine with formic acid (see below). 3. *as*-Phenylhydrazido-acetic ester and  $\text{KCNO}$  give 1-phenyl-semicarbazide-1-acetic ester,  $\text{PhN}(\text{CH}_2\text{CO}_2\text{R})\text{NHCONH}_2$ , which is hydrolysed to *N*-phenyl-diketo-hexahydro- $\alpha$ -triazine.

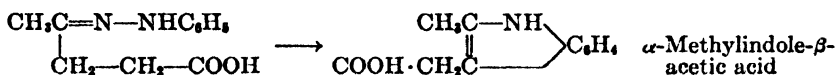
4, 5, 6. The phenylhydrazino-carboxylic acids which correspond to  $\beta$ -hydroxy-acids anhydride very readily (formation of *pyrazolidones* and *lactazams*), and in many cases cannot be isolated.



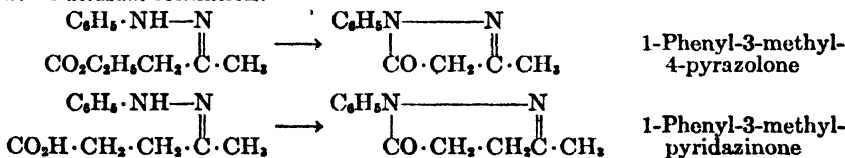
**MONOKETONIC ACID DERIVATIVES OF PHENYLHYDRAZINE.** The esters of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -ketocarboxylic acids react with phenylhydrazine in a similar manner to the ketones, with formation of phenylhydrazones. Phenylhydrazones of free  $\alpha$ - and  $\gamma$ -ketocarboxylic acids are also known. Those of the esters give indole derivatives on treatment with  $\text{ZnCl}_2$  or  $\text{H}_2\text{SO}_4$ , like the keto-hydrazones (p. 154). Those of  $\beta$ - and  $\gamma$ -ketocarboxylic esters and free  $\gamma$ -ketocarboxylic acids readily give lactazams. **Laevulinic acid phenylhydrazone** (Vol. I, p. 480) gives 1-phenyl-3-methyl-pyridazonone, and under other conditions,  $\alpha$ -methylindole- $\beta$ -acetic acid. **Acetoacetic ester phenylhydrazone**,  $\text{PhNH} \cdot \text{N} \cdot \text{C}(\text{CH}_3)=\text{CH}_2 \cdot \text{CO}_2\text{Et}$ , m.p.  $50^\circ$ , obtained by the action of phenylhydrazine on acetoacetic ester (*Walker*, *Am. Chem. J.* 16, 430) spontaneously changes into 1-phenyl-3-methyl-pyrazolone (Vol. IV), but with acetyl chloride, or an excess of  $\text{HCl}$  into 1-phenyl-3-methyl-5-ethoxy-pyrazole (Vol. IV).

*Formation of heterocyclic compounds from phenylhydrazones of ketonic acids.*—

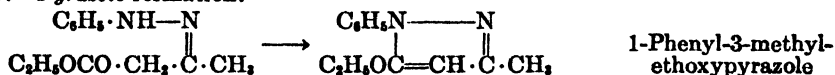
1. Indole condensation (p. 154):



2. Lactazam formation:



3. Pyrazole formation:



**PHENYLHYDRAZINE DERIVATIVES OF CARBONIC ACID.** If an aqueous emulsion of phenylhydrazine is saturated with carbon dioxide, **phenylhydrazine phenylcarbazinate**,  $\text{PhNHNH} \cdot \text{COO}(\text{NH}_2\text{NHPh})$  is formed as a white mass of crystals (*E. Fischer*, *Ann.* 190, 123; *Freundler*, *Bull.* [3], 25, 859). **Ethyl phenylcarbazinate**,  $\text{PhNHNHCOOEt}$ , m.p.  $86^\circ$ , is obtained by the action of  $\text{ClCOOEt}$  on an ethereal solution of phenylhydrazine; at  $240^\circ$  it loses alcohol and **diphenylurazine** (Vol. IV) is formed (*Heller*, *Ann.* 263, 278; *Peratoner*, *Ber.*

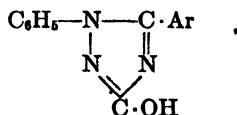
26, R 20). *α*s-Phenylhydrazino-formic ester,  $\text{PhN}(\text{NH}_2)\text{COOEt}$ , an oil, is obtained from its aceto-compound, which is formed by the action of chloroformic ester on phenylhydrazine acetate, (*Rupe*, Ber. 29, 839; 32, 10), and on continued treatment with chloroformic ester gives phenylhydrazino- $\alpha$ , $\beta$ -dicarboxylic ester,  $\text{PhN}(\text{COOEt})\text{NH}\cdot\text{COOEt}$ , m.p. 59°. With  $\text{COCl}_2$  it gives diphenyl-carbazide-dicarboxylic ester,  $\text{CO}[\text{NH}\cdot\text{N}(\text{Ph})\text{COOEt}]_2$ , m.p. 159°.  $\alpha$ - and  $\beta$ -Cyanophenylhydrazines,  $\text{Ph}(\text{CN})\text{N}\cdot\text{NH}_2$ , m.p. 89°, and  $\text{PhNH}\cdot\text{NHCN}$ , an unstable oil, are formed together by the action of cyanogen bromide on phenylhydrazine (*Pelizzari*, Gazz. 41, I, 54). The  $\alpha$ -compound is hydrolysed to  $\alpha$ -phenyl semicarbazide, carbamic  $\alpha$ -phenylhydrazide,  $\text{NH}_2\text{NPh}\cdot\text{CONH}_2$ , m.p. 120°.  $\beta$ -Phenyl semicarbazide,  $\text{PhNHNHCONH}_2$ , m.p. 172°, is obtained by the action of potassium cyanate on salts of phenylhydrazine (*E. Fischer*, Ann. 190, 113), or by heating phenylhydrazine with urea or urethane; when heated it is converted into phenyl-urazol and diphenyl-urazine, with liberation of  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{NH}_3$ , and benzene. It is converted into phenyl azide by the action of potassium hypochlorite (Ber. 40, 3033). Phenyl semicarbazide gives oxadiazolone compounds with  $\text{COCl}_2$ ,  $\text{CSCl}_2$ , and  $\text{PhNCCl}$  (*Freund*, Ber. 26, 287) in the same way as sym-acetophenylhydrazine (p. 000). For the nitroso-compound see p. 165. For homologous aryl semicarbazides see *Michael*, Am. Chem. J. 20, 377; *Young*, J. 73, 368.

$\beta$ -*m*-Tolyl semicarbazide,  $\text{MeC}_6\text{H}_4\text{NHNHCONH}_2$ , m.p. 184°, obtained from *m*-tolyl-hydrazine and urea, is used as an antipyretic (Ger. Pats. 157,572 and 163,037).

2,4-Diphenyl semicarbazide, phenylcarbamic acid- $\alpha$ -phenylhydrazide,  $\text{PhNH}\cdot\text{CO}\cdot\text{N}(\text{Ph})\text{NH}_2$ , m.p. 165°, is best obtained from phenyl dithiocarbazine ester,  $\text{PhNHNHCSSMe}$  (p. 159) by combining it with  $\text{PhCNO}$ , giving  $\text{PhNHCON}\cdot\text{Ph}\cdot\text{NHCSSMe}$ , converting this substance into the dimethyl ester,  $\text{PhNHCON}\cdot\text{Ph}\cdot\text{N}:\text{C}:(\text{SMe})_2$ , by means of methyl iodide and alkali, and finally decomposing this with dilute sulphuric acid. When 2,4-diphenyl semicarbazide is heated above its m.p. it isomerises to 1,4-diphenyl semicarbazide, phenylcarbamic acid- $\beta$ -phenylhydrazide,  $\text{PhNHCONHNHPh}$ , m.p. 176°, which differs from its isomer in forming an azo-compound with ferric chloride (*Busch*, Ber. 36, 1362).

2,4,4-Triphenyl semicarbazide,  $\text{Ph}_2\text{NCO}\cdot\text{N}(\text{Ph})\text{NH}_2$ , m.p. 128°, is obtained as its aceto-compound from diphenyl-carbamyl chloride and  $\beta$ -aceto-phenylhydrazine (*Rupe*, Ber. 33, 246).

sym-Phenyl-carbohydrazide, dianilino-urea ("diphenyl carbazide"),  $(\text{PhN}\cdot\text{H}\cdot\text{NH})_2\text{CO}$ , m.p. 175°, is obtained by heating urethane or phenyl carbonate with phenylhydrazine, or by adding phosgene drop by drop to an ethereal solution of phenylhydrazine (*Skinner*, Ber. 20, 3372; *Heller*, Ann. 263, 277; *Cazeneuve*, C.r. 129, 1254). In acetic acid, and in the presence of anhydrous sodium acetate, it condenses with aromatic aldehydes forming 1-phenyl-3-hydroxy-1,2,4-triazoles, substituted in the 5-position in addition to aniline (*Oddo*, Gazz. 45, I, 238):



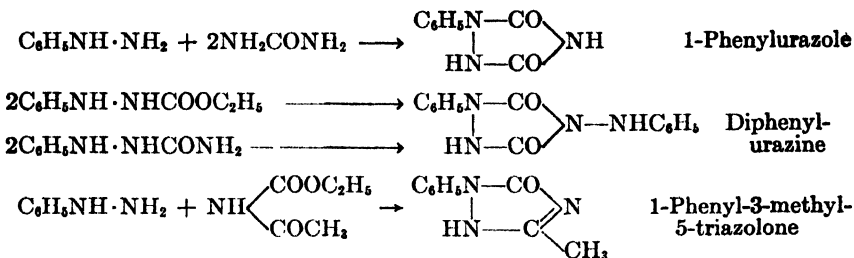
On boiling with alcoholic potash, or by the action of copper or mercury salts it loses 2H and is converted into salts of diphenyl-carbazone,  $\text{PhN}:\text{NCONHNHPh}$ , orange-red needles, m.p. 157° (decomp.) (*Heller*, Ann. 263, 274). The metallic salts of diphenyl-carbazone,  $\text{PhN}_2\text{CONXNHPh}$ , are red to blue in colour, and are more or less explosive. It dyes silk and wool in a neutral bath. In forming salts

it probably rearranges into a C-hydroxy-formazyl,  $\text{HO}\cdot\text{C} \begin{array}{l} \nearrow \text{N}:\text{NHPh} \\ \searrow \text{N}:\text{NPh} \end{array}$  (*Bamberger*,

Ber. 44, 3743). Like diphenyl-carbazide it is oxidised by silver acetate to diphenyl-carbodiazone,  $(\text{PhN}:\text{N})_2\text{CO}$ , colourless needles, decomp. on heating, and regenerating the K-salt of diphenyl-carbazone on boiling with alcoholic potash (*Cazeneuve*, C.r. 132, 412; Bull. [3], 25, 758; *Feigl*, Mo. 45, 63). Diphenyl-carbohydrazide and carbazone are used in analysis as reagents for mercury (*Trülek*, Coll. Czech. 1933).

**CYCLIC DERIVATIVES OF UREA AND CARBAMIC ACID.** Phenyl-urazole (Vol. IV) is obtained from phenyl-semicarbazide on heating, from phenylhydrazine hydrochloride by the action of urea, and from biuret by the action of phenylhydrazine. Diphenyl-urazine is formed on heating the ethyl ester of phenylthiocarbazine acid, or by heating phenyl semicarbazide.

1-Phenyl-3-methyl-5-triazolone (Vol. IV) is obtained by the action of acetylurethane on phenylhydrazine.



**PHENYLHYDRAZINE DERIVATIVES OF THIOCARBONIC ACID.** When carbon disulphide is added to a solution of phenylhydrazine in ether, phenylhydrazine phenyldithiocarbazine,  $(\text{PhNH}\cdot\text{NH}\cdot\text{CSS})(\text{NH}_2\text{NHPh})$ , m.p.  $96^\circ$ , is obtained. The free phenyl-dithiocarbazine acid is precipitated from solutions of its salts by mineral acids in the form of fine, shining flakes, which are easily oxidised to the disulphide (*E. Fischer*, Ann. 190, 114). Mono- and di-alkyl esters can be obtained by the action of alkyl halides and alkali on the acid. They are derived partially from tautomeric forms, and correspond to the formulae  $\text{PhN}\cdot\text{HN}:\text{C}(\text{SMe})\text{SH}$ ,  $\text{PhNHN}:\text{C}(\text{SMe})_2$ , and  $\text{PhNHN}:\text{C} \begin{array}{l} \diagup \text{S}-\text{CH}_2 \\ \diagdown \text{S}-\text{CH}_2 \end{array}$ .

When two different radicals are introduced, stereoisomeric forms of compounds  $\text{PhNH}\cdot\text{N}:\text{C} \begin{array}{l} \diagup \text{SR} \\ \diagdown \text{SR}' \end{array}$  arise. The configuration of these compounds, which may also be regarded as phenylhydrazones of mixed dithiocarbonic esters, has been determined by Busch (J. pr. 93, 25). Dilute acids decompose the dialkyl esters (Vol. I, p. 485; Busch, Ber. 34, 1119; J. pr. 65, 473). When the potassium salt of phenylthiocarbazine acid is treated with carbonyl chloride or carbon disulphide, N-phenyl-thiobiazolone-hydrosulphide and N-phenyl-dithiobiazolone-hydrosulphide (p. 160) are formed.

$\alpha$ -Phenyl-thio-semicarbazide, thiocarbamic- $\alpha$ -phenylhydrazide,  $\text{NH}_2\cdot\text{NPhC}\cdot\text{S}\cdot\text{NH}_2$ , m.p.  $153^\circ$ , is produced by the action of ammonium hydrosulphide on  $\alpha$ -cyano-phenylhydrazine.  $\beta$ -Phenyl-thio-semicarbazide, thiocarbamic- $\beta$ -phenylhydrazide,  $\text{PhNH}\cdot\text{NH}\cdot\text{CSNH}_2$ , m.p.  $200^\circ$ , isomeric with phenyl-thio-semicarbazide,  $\text{PhNH}\cdot\text{CSNHNH}_2$  (p. 96) is produced by a rearrangement of phenylhydrazine thiocyanate at  $160$ – $170^\circ$ , and changes into thiocarbazine or benzodiazthine (p. 160) when heated with HCl (*Harries*, Ber. 27, 861).

2,4-Diphenyl-thio-semicarbazide, phenyl-thiocarbamic- $\alpha$ -phenylhydrazide,  $\text{PhNHCSN}\cdot\text{PhNH}_2$ , m.p.  $139^\circ$ , is formed by the action of aniline on phenyl-dithiocarbazine acid, or by the combination of phenyl mustard oil with phenylhydrazine. Like 2,4-diphenyl-semicarbazide (p. 158), but much more readily, one phenyl group migrates and the substance changes into

1,4-Diphenyl-thio-semicarbazide, phenyl-thiocarbamic- $\alpha$ -phenylhydrazide,  $\text{PhNHCSNHNHPh}$ , m.p.  $176^\circ$ . The two isomers yield isomeric methyl ethers,  $\text{PhN}:\text{C}(\text{SMe})\text{NPhNH}_2$  and  $\text{PhN}:\text{C}(\text{SMe})\cdot\text{NHNHPh}$ , respectively, with methyl iodide and alkali. The 2,4-compound reacts readily with benzaldehyde and yields a benzylidene derivative, while the 1,4-compound does not react in this manner. For further reactions of these isomers, see Busch, Ber. 34, 320.

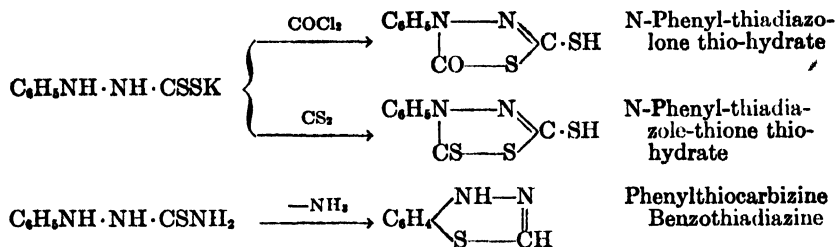
Diphenyl-thiocarbazine, sym-diphenyl-thio-carbohydrazide,  $(\text{PhNH}\cdot\text{NH})_2\text{CS}$ , forms colourless needles melting at  $150^\circ$  to a green liquid. It is produced when phenylhydrazine phenyl-thiocarbazine is heated to  $100$ – $110^\circ$  (*E. Fischer*, Ann. 190, 118).



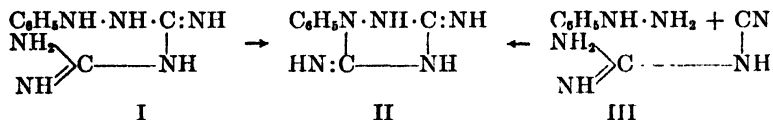
**Diphenyl-thiocarbazon**,  $\text{PhN}=\text{N} \cdot \text{CSNH} \cdot \text{NHPh}$ , bluish-black crystals, is formed when diphenyl-thiocarbazide is boiled for a short time with fairly concentrated alcoholic potash. The compound is used under the name "dithizone" for the determination of lead and copper (*Fischer, Angew. Ch.* 47, 685, etc.).

**Diphenyl-thiocarbodiazone**,  $(\text{PhN}=\text{N})_2\text{CS}$ , obtained by oxidising diphenyl-thiocarbazon with hydrated manganese dioxide, forms small red needles (*Ann.* 212, 316).

*Formation of heterocyclic compounds from phenylhydrazine derivatives of thiocarbonic acid.*



*Phenylhydrazine derivatives of guanidine.*—**Anilino-guanidine**,  $\text{NH}:\text{C}(\text{NH}_2) \cdot \text{NHNHPh}$  and **amino-phenylguanidine**,  $\text{NH}:\text{C}(\text{NH}_2) \cdot \text{N}(\text{Ph})\text{NH}_2$ , are formed together by the action of phenylhydrazine on cyanamide (*Pellizzari, Gazz.* 26, II, 179; 31, I, 513). Under other conditions a phenylhydrazine derivative of biguanide is formed, viz., the unstable *anilino-biguanide*,  $\text{PhNH} \cdot \text{NH} \cdot \text{C}:(\text{NH}) \cdot \text{NH} \cdot \text{C}:(\text{NH}) \cdot \text{NH}_2$  (I). On heating with cyanamide, this becomes *N-phenylguanazole* (II), which is also obtained from *dicyano-diamide* (III) by the action of phenylhydrazine.

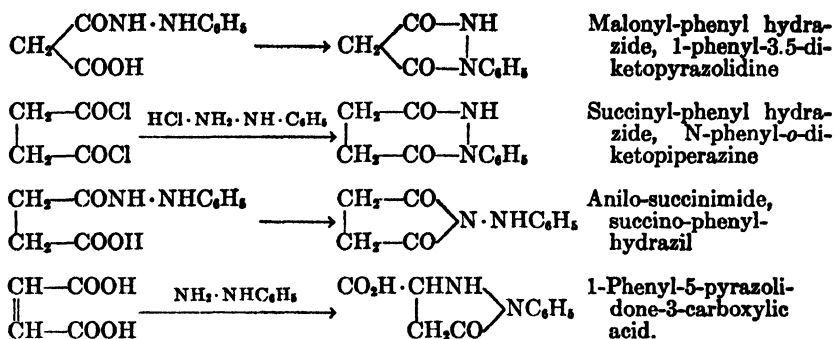


**Dianilino-guanidine**,  $\text{NH}:\text{C}(\text{NH} \cdot \text{NHPh})_2$ , hydrobromide, m.p. 180°, is a by-product in the action of cyanogen bromide on phenylhydrazine (p. 148) (*Pellizzari, Ber.* 24, R 649; *Schall, J.* pr. 61, 440).

**PHENYLHYDRAZINE DERIVATIVES OF DICARBOXYLIC ACIDS.** **Oxalophenylhydrazilic acid**,  $\text{PhNH} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , m.p. 110° (*Bülow, Ann.* 236, 197), and **oxalo-phenylhydrazide**,  $(\text{PhNH} \cdot \text{NH} \cdot \text{CO})_2$ , m.p. 278°, correspond to *oxanilic acid* and *oxanilide*. From malonic acid are derived: **malonic mono-ester phenylhydrazide**,  $\text{Ph} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOEt}$ , m.p. 90°, obtained from malonyl chloride and phenylhydrazine. It dissolves readily in caustic potash, and from this solution HCl precipitates **malonyl-phenyl-hydrazide**, **1-phenyl-3,5-diketopyrazolidine** (formula below). Malonamide and phenylhydrazine at 200° give **malonyl-diphenyl-hydrazide**  $(\text{PhNH} \cdot \text{NH} \cdot \text{CO})_2\text{CH}_2$ , m.p. 187° (*Michaelis, Ber.* 25, 1550). *Ethylene succinic acid* forms compounds corresponding to those of malonic acid. **Succinyl-phenyl-hydrazilic ester**, m.p. 107°. **Succinyl phenyl-hydrazide** (see below) is obtained from phenylhydrazine hydrochloride and succinyl chloride. **Succinyl-diphenyl-hydrazide**,  $(\text{CH}_2\text{CO} \cdot \text{NH} \cdot \text{NHPh})_2$ , m.p. 201° (*Freund, Ber.* 21, 2462) and **anil-succinimide**,  $(\text{CH}_2\text{CO})_2\text{NNHPh}$ , see below.

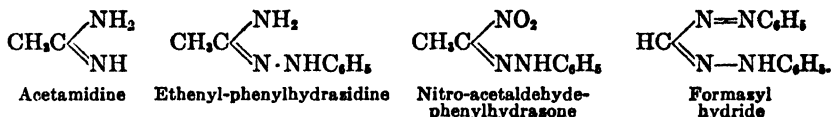
**PHENYLHYDRAZINE DERIVATIVES OF UNSATURATED DICARBOXYLIC ACIDS AND HYDROXY-CARBOXYLIC ACIDS.** **Maleic phenyl-hydrazide** is obtained from maleic anhydride and phenylhydrazine. With boiling aqueous maleic or fumaric acid and excess phenylhydrazine, an addition reaction takes place with subsequent lactam formation, and **1-phenyl-5-pyrazolidone-3-carboxylic acid** (Vol. IV) is formed (*Duden, Ber.* 26, 117). A similar reaction occurs with acrylic and crotonic acids.

*Formation of heterocyclic compounds from phenylhydrazine derivatives of dicarboxylic acids* (see also Vol. IV).



*Phenylhydrazidines or Amidrazones. Nitrazones.*  
*Phenylhydrazo-aldoximes. Phenylazo-aldoximes (Nitrosozones).*  
*Formazyl Compounds*

Some groups of compounds of the amidine type are related to the carboxylic derivatives of phenylhydrazine, and should be dealt with here. The hydrazidines are amidines in which the imino-group is replaced by the phenylhydrazone group; in the nitrazones and in the formazyl compounds, there is a further replacement of the amino-group by the nitro- and azophenyl-groups, respectively:



To these must be added the phenylazo-aldoximes, the stable isomeric products of the very unstable nitroso-phenylhydrazones:



**A. PHENYLHYDRAZIDINES OR AMIDRAZONES.** The hydrochloride of ethenyl-phenylhydrazidine,  $\text{CH}_3\text{C} \begin{cases} \text{N} \cdot \text{NHPh} \\ \text{NH}_2 \end{cases}$ , is formed by the interaction of phenylhydrazine and the hydrochloride of acetimino-ether (Pinner, Ber. 17, 2002).

Cyan-amidrazone or dicyano-phenylhydrazine,  $\text{NC}-\text{C} \begin{cases} \text{N} \cdot \text{NHPh} \\ \text{NH}_2 \end{cases}$ , m.p. 160°

(decomp.), and diamidrazone or cyano-phenylhydrazine,  $\left( \begin{smallmatrix} \text{Ph} \cdot \text{NH} \cdot \text{N} \\ \text{NH}_2 \end{smallmatrix} \text{C} \right)_2$ ,

m.p. 225°, are formed by the action of cyanogen on phenylhydrazine. The dicyano-compound is also obtained by reducing the addition product of diazo-benzene cyanide (p. 121) and HCN, which presumably has the structure  $\text{Ph} \cdot \text{N}:\text{N} \begin{cases} \text{NH} \\ \text{CN} \end{cases}$  (Hantzsch, Ber. 28, 2082; Nef. Ann. 287, 300). The constitutions of

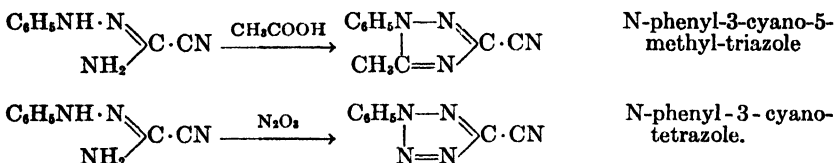
cyanamidrazone and diamidrazone are deduced from the fact that the former is produced from flaveanic acid,  $\text{NC}-\text{C} \begin{cases} \text{S} \\ \text{NH}_2 \end{cases}$ , and the latter from rubeanic acid,

$\text{NH}_2\text{C}(\text{S})=\text{C}(\text{S})\text{NH}_2$ , (Vol. I, p. 541) and from oxalo-diaminoxime,

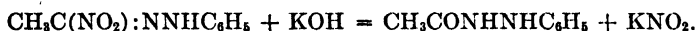
$\text{HON}=\text{C}(\text{NH}_2)=\text{C}(\text{NOH})\text{NH}_2$ , by the action of phenylhydrazine (Bamberger, Ber. 26, 2385). Diamidrazone is also obtained by reduction of diformazyl (p. 164).

**Acetyl-amidrazone, pyruvic phenylhydrazidine**,  $\text{CH}_3\text{CO}\cdot\text{C}(\text{NH}_2)=\text{N}\cdot\text{NHPh}$ , m.p. 182°, is obtained from formazyl-methyl ketone (p. 164) by reduction with ammonium sulphide (Bamberger, Ber. 26, 2783).

**Formation of heterocyclic compounds with amidrazones.**—The amidrazones condense with carboxylic acids, anhydrides or chlorides to form heterocyclic triazole derivatives, and with nitrous acid to form tetrazole derivatives. Cyanamidrazone gives N-phenyl-3-cyano-5-methyl-triazole with acetic anhydride, and N-phenyl-3-cyano-tetrazole with nitrous acid (Vol. IV):



**B. THE NITROHYDRAZONES OR NITRAZONES.** These are the nitro-compounds corresponding to the amidrazones. They are obtained from the alkali salts of primary nitroparaffins (Vol. I, p. 178) by the action of diazonium salts, and were formerly thought to be nitro-azoparaffins (p. 138); presumably, however, the free compounds are nitro-hydrazones, and their metallic salts and O-alkyl ethers are derived from a tautomeric form, a phenyl-azo-nitro-acid,  $\text{RC}(\text{NOOH})=\text{N}\cdot\text{NPh}$ . They are readily decomposed by alkalis to nitrites and  $\beta$ -acidyl-phenylhydrazides (Bamberger, Ber. 31, 2626):

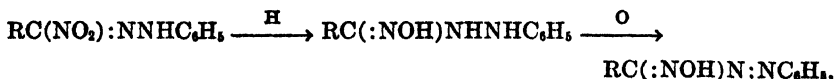


Some poly-halogeno-diazo-compounds combine with primary nitroparaffins in the molecular proportion 2:1 with the formation of mixed azo-compounds (Bamberger, Ber. 36, 3833).

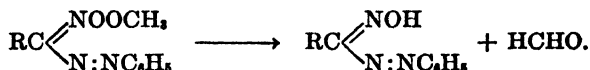
**Nitroformaldehyde-phenylhydrazine**,  $\text{HC}(\text{NO}_2):\text{N}\cdot\text{NHPh}$ , exists in two forms:  $\alpha$ -, m.p. 75°, and  $\beta$ -, m.p. 85°. With diazomethane it forms an unstable O-methyl ether,  $\text{HC}(\text{NOOMe})\text{N}\cdot\text{NPh}$ , m.p. 54°, but with MeI or NaOMe a N-methyl derivative results, of the formula  $\text{HC}(\text{NO}_2):\text{NNMe}\cdot\text{Ph}$ , m.p. 92°; the latter, on reduction, gives *phenyl-methyl-formhydrazidine*,  $\text{HC}(\text{NH}_2):\text{NNMe}\cdot\text{Ph}$ , m.p. 101°, and, in addition, methylamine and *as*-phenyl-methylhydrazine (Bamberger, Ber. 34, 574).

**Nitro-acetaldehyde-phenylhydrazine**,  $\text{CH}_3\text{C}(\text{NO}_2):\text{NNHPh}$ , small yellow leaflets, m.p. 142°. The compound gives an O-methyl ether,  $\text{CH}_3\text{C}(\text{NOOMe})\text{N}\cdot\text{NPh}$ , m.p. 68° with diazomethane.

**C. PHENYLHYDRAZO-ALDOXIMES AND PHENYL-AZO-ALDOXIMES OR NITROSAZONES**, are obtained by the following methods: (1) When nitrazones are reduced with alcoholic ammonium sulphide, phenylhydrazo-aldoximes are formed, and these are readily oxidised by ferric chloride to form phenylazo-aldoximes:



(2) When boiled with water the O-methyl ethers of nitrazones (see above) suffer direct dissociation into formaldehyde and phenylazo-aldoximes:



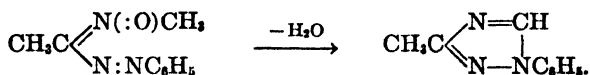
(3) When aldehyde-phenylhydrazones are treated with amyl nitrite and sodium ethylate or pyridine, the first stage of the reaction probably consists in the formation of very unstable nitrosohydrazones (nitrosazones), which readily rearrange to azo-aldoximes (Bamberger, Ber. 35, 54, 108; 36, 53, 86, 347):



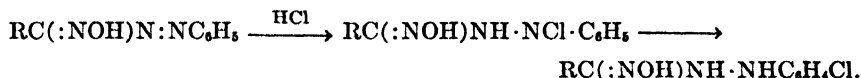
The aryl-hydrazones of glyoxylic acid lose carbon dioxide when acted upon by nitrous acid, and are converted into phenylazo-aldoximes (Busch, J. pr. 71, 366).

**Phenylhydrazo-formaldoxime**,  $\text{HC(:NOH)NH}\cdot\text{NHPh}$ , white needles, m.p.  $113^\circ$ , is obtained from nitro-formaldehydehydrazone by the action of alcoholic ammonium sulphide, and, on oxidation with ferric chloride, gives **phenylazo-formaldoxime**,  $\text{HC(:NOH)N:NPh}$ , golden-yellow needles, m.p.  $94^\circ$  (decomp.).

**Phenylhydrazo-acetaldoxime**,  $\text{CH}_3\text{C(:NOH)NHNHPh}$ , m.p.  $128^\circ$ , obtained from nitro-acetaldehydehydrazone, gives **phenylazo-acetaldoxime**,  $\text{CH}_3\text{C(:NOH)N:NPh}$ , m.p.  $118^\circ$ , on oxidation. The latter is also obtained: by boiling the O-methyl ether of nitro-acetaldehydehydrazone (see above) with water; by treating acetaldehyde-phenylhydrazone or benzene-azoethane (p. 138) with amyl nitrite and sodium ethoxide or pyridine; and finally from acetaldehyde-ammonia and nitroso-phenylhydrazine (Voswinckel, Ber. 35, 1009). With methyl iodide, its silver salt gives an O-methyl ether of the formula  $\text{CH}_3\text{C(:NOMe)N:NPh}$ , an oil, b.p.  $134^\circ$  (12 mm.), but its sodium salt gives an N-methyl ether, m.p.  $96^\circ$  with methyl iodide. Under the influence of sodium ethoxide, the latter readily condenses with ring closure, and forms *phenyl-methyl-triazole*:



The phenylazo-aldoximes add on hydrogen chloride and form chlorophenylhydrazo-aldoximes, a migration of the chlorine atom into the benzene nucleus taking place:



**D. FORMAZYL COMPOUNDS** are highly coloured substances, usually red. They crystallise readily, and their sulphonic acids are dyes (cf. formazyl-benzene-sulphonic acids, Fichter, Ber. 33, 747). They are obtained: (1) from phenylhydrazones and normal diazonium salts, usually in alkaline solution; (2) from phenylhydrazine and phenylhydrazides, with the intermediate formation of hydrazone-hydrazides, which are oxidised by phenylhydrazine, losing two hydrogen atoms; and (3) from phenylhydrazine and phenylhydrazide chlorides corresponding to imido-chlorides (Pechmann, Ber. 27, 320; Bamberger, Ber. 29, 1386).

**Formazyl-hydride**,  $\text{HC} \begin{array}{l} \diagup \text{N:NPh} \\ \diagdown \text{N:NHPh} \end{array}$ , m.p.  $119^\circ$ , is obtained from diazonium

acetate and malonic acid, by fusing formazyl-carboxylic acid, or from its acetylation product, *acetyl-formazyl-hydride*,  $\text{CH(N}_2\text{Ph):NN(COCH}_3\text{)Ph}$ , by the action of methyl-alcoholic potash (Bamberger, J. pr. 65, 131).

**C-Nitro-formazyl**,  $\text{NO}_2\cdot\text{C} \begin{array}{l} \diagup \text{N:NHPh} \\ \diagdown \text{N:NPh} \end{array}$ , m.p.  $156^\circ$ , obtained from diazonium

solutions by the action of alkaline nitromethane, is a formazyl and a nitrazone derivative at one and the same time. It is reduced by sodium sulphide to

**C-amino-formazyl**,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \diagup \text{N} \cdot \text{NHPh} \\ \diagdown \text{N} \cdot \text{NPh} \end{smallmatrix}$ , m.p. 135–136° (dec.), which crystallises with one molecule of alcohol in dark-red flakes with a metallic lustre (*Bamberger*, *Ber.* 33, 2043; *Ann.* 446, 280).

**Methyl-formazyl**, *formazyl-methane*,  $\text{MeC}(\text{N}_2\text{Ph}) : \text{NNHPh}$ , m.p. 123°, is obtained from acetaldehyde phenylhydrazone or pyruvic-phenylhydrazone by the action of an alkali phenyl-diazotate (*Bamberger*, *Ber.* 36, 87; *J. pr.* 64, 213).

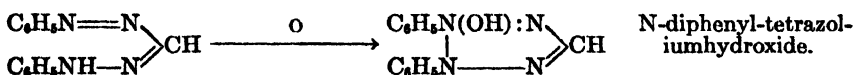
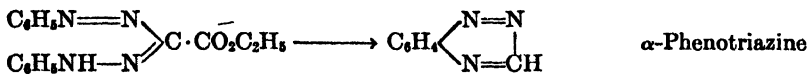
**Formazyl-methyl-ketone**,  $\text{Me} \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \diagup \text{N} \cdot \text{NHPh} \\ \diagdown \text{N} \cdot \text{NPh} \end{smallmatrix}$ , m.p. 134°, is obtained from acetone, acetoacetic acid, pyruvic aldehyde phenylhydrazone, or benzene-azo-acetyl-acetone by the action of a phenyl diazonium salt (*Bamberger*, *Ber.* 25, 3211).

**Formazyl-carboxylic acid**,  $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \diagup \text{N} \cdot \text{NPh} \\ \diagdown \text{N} \cdot \text{NHPh} \end{smallmatrix}$ , m.p. 158° (decomp.), is obtained by the hydrolysis of **ethyl formazyl-carboxylate**, m.p. 117°, which is formed by the interaction of phenyldiazonium chloride with acetoacetic ester, or oxalo-acetic ester, or the phenylhydrazone of mesoxalic hydrogen ester (*Bamberger*, *J. pr.* 65, 123). **Diformazyl**,  $\text{PhNH} \cdot \text{N} \begin{smallmatrix} \diagup \text{C} \begin{smallmatrix} \diagup \text{N} \cdot \text{NPh} \\ \diagdown \text{N} \cdot \text{NHPh} \end{smallmatrix} \\ \diagdown \text{C} \begin{smallmatrix} \diagup \text{N} \cdot \text{NPh} \\ \diagdown \text{N} \cdot \text{NHPh} \end{smallmatrix} \end{smallmatrix}$ , m.p. 226°, is

obtained as greenish-brown, shining leaflets, by the action of a diazonium salt on laevulic, hydrochelidonic, or acetone-diacetic acids, or the osazone of dihydroxy-tartaric acid. **Formazyl-acrylic acid**,  $\text{CO}_2\text{H} \cdot \text{CH} : \text{CH} \cdot \text{C} \begin{smallmatrix} \diagup \text{N} \cdot \text{NPh} \\ \diagdown \text{N} \cdot \text{NHPh} \end{smallmatrix}$ , m.p. 199° (decomp.), is obtained by the action of glutacetic acid on phenyldiazonium acetate (*Henrich*, *Ber.* 40, 4927).

**Formazyl-azobenzene**, **phenylazoformazyl**,  $(\text{PhN} : \text{N})_2\text{C} : \text{N} \cdot \text{NHPh}$ , m.p. 162°, is obtained from formazyl-carboxylic acid, or the phenylhydrazone of glyoxylic acid or of acetaldehyde, by the action of a diazonium salt in alkaline solution (*Bamberger*, *J. pr.* 64, 199). By the action of an alkali phenyl-diazotate on pyruvic acid, **formazyl-glyoxylic acid**,  $\text{COOH} \cdot \text{CO} \cdot \text{C}(\text{N}_2\text{Ph}) : \text{N} \cdot \text{NHPh}$ , m.p. 166°, is first formed, and on prolonged action of the diazotate is decomposed into oxalic acid and phenyl-azo-formazyl (*Bamberger*, *J. pr.* 64, 204).

**Formation of heterocyclic compounds from formazyl compounds.**—Under the influence of strong mineral acids, the formazyl compounds lose aniline and form **phenotriazine** derivatives; thus, formazyl-carboxylic ester gives  $\alpha$ -phenotriazine (Vol. IV). On oxidation of formazyl compounds, tetrazolium compounds are formed, e.g., from formazyl hydride, N-diphenyl-tetrazolium hydroxide is obtained (Vol. IV).



(q) **PHENYL-NITROSOHYDRAZINE**,  $\text{C}_6\text{H}_5\text{N} \begin{smallmatrix} \diagup \text{NO} \\ \diagdown \text{NH}_2 \end{smallmatrix}$  or  $\text{PhNHNHNO}$ ,

forms brownish-yellow crystalline flocks, which readily change to phenyl azide (p. 132). It is produced from phenylhydrazine and nitrous acid, but an excess of the latter oxidises it to phenyl-diazonium nitrate (*Fischer*, *Ann.* 190, 89; *Allschul*, *C.* 1897, I, 381; *Rugheimer*, *Ber.* 33, 1718). The first of the above formulae is supported by the fact that the nitroso-phenylhydrazones of aldehydes (see below), which possess the formula  $\text{Ph} \cdot \text{N}(\text{NO})\text{N} : \text{CH} \cdot \text{R}$ , rearrange themselves into derivatives of dihydrotetrazene (*Busch*, *Ber.* 49, 317). When heated in indifferent solvents, phenyl-nitrosohydrazine decomposes into nitrous oxide and aniline (*Thiele*,

Ber. 41, 2809). On reduction it is decomposed and phenylhydrazine is reformed. The nitroso-derivatives of alkylated phenylhydrazines behave similarly: thus, nitroso- $\alpha, \beta$ -diethyl-phenylhydrazine,  $\text{PhN}(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_5)\text{NO}$ , gives ethylaniline and ethylhydrazine (Harries, Ber. 36, 202). On the other hand, nitroso-formyl-phenylhydrazine,  $\text{PhN}(\text{NO})\text{NHCHO}$ , m.p.  $85^\circ$  (decomp.) and nitroso-acetyl-phenylhydrazine,  $\text{PhN}(\text{NO})\text{NHCOCH}_3$ , m.p.  $63^\circ$  (decomp.), give, on reduction with sodium amalgam and alcohol, derivatives of the hypothetical phenyl-triazane  $\text{PhN}(\text{NH}_2)_2$ , which have been isolated as their benzylidene compounds: benzylidene-formyl-phenyltriazane,  $\text{PhN}(\text{N}:\text{CHPh})\text{NH}\cdot\text{CHO}$ , m.p.  $183^\circ$  (decomp.) and benzylidene-acetyl-phenyltriazane,  $\text{PhN}(\text{N}:\text{CHPh})\text{NH}\cdot\text{COCH}_3$ , m.p.  $163^\circ$  (decomp.) (Wohl, Ber. 35, 1900). Nitrosophenyl-semicarbazide,  $\text{PhN}(\text{NO})\text{NHCONH}_2$ , m.p.  $127^\circ$  (decomp.), obtained from  $\beta$ -phenyl-semicarbazide by the action of sodium nitrite and acetic acid, decomposes slowly even at ordinary temperature, and more rapidly on heating, with the formation of phenyl-azocarboxylic amide (p. 138); on boiling with caustic potash, it forms phenyl azide (Widmann, Ber. 28, 1925).

(r<sub>1</sub>) TETRAZENES, or TETRAZONES, derived from the hypothetical nitrogen hydride,  $\text{NH}_2\text{—N=N—NH}_2$ , are produced by the oxidation of *as*-alkyl-phenyl- or diphenyl-hydrazines, with mercuric oxide in alcoholic or ethereal solution, or with hypochlorous acid, bromine, or a dilute solution of ferric chloride (Wieland, Ber. 43, 3260).



They are solids which decompose on melting, or on boiling with dilute acids. Dimethyl-diphenyl-tetrazene,  $\text{Ph}\cdot\text{N}(\text{CH}_3)_2\cdot\text{N}_2\cdot\text{N}(\text{CH}_3)_2\cdot\text{Ph}$ , m.p.  $137^\circ$ . Diethyl-diphenyl-tetrazene, m.p.  $108^\circ$  (Michaelis, Ann. 252, 281). Tetraphenyl-tetrazene,  $\text{Ph}_2\text{N}\cdot\text{N}_2\cdot\text{NPh}_2$ , m.p.  $123^\circ$ , is obtained from *as*-diphenyl-hydrazine. Tetra-*p*-tolyl-tetrazene,  $(\text{CH}_3\text{C}_6\text{H}_4)_2\text{N}\cdot\text{N}_2\cdot\text{N}(\text{C}_6\text{H}_4\text{CH}_3)_2$ , a compound existing as fiery yellow needles, m.p.  $134^\circ$  (decomp.) is obtained by oxidising *as*-*p*-ditolyl-hydrazine in acetone solution with potassium permanganate. When heated in indifferent solvents, the quaternary tetrazenes decompose into nitrogen and tetra-aryl-hydrazines. They dissolve in concentrated acids with an intensely blue colour, nitrogen being evolved. The reaction products are the same as those obtained from the corresponding tetra-aryl-hydrazines (p. 149) (Wieland, Ber. 41, 3502; Ann. 392, 133).

(r<sub>2</sub>) TETRAZANES, or HYDROTETRAZONES, derived from the hypothetical nitrogen hydride  $\text{NH}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{NH}_2$ , have been obtained by oxidising aldehyde-phenylhydrazones with mercuric oxide or amyl nitrite (Mumanni, Gazz. 22, II, 21; Pechmann, Ber. 27, 2920; Busch, Ber. 49, 310). Thus dibenzyl-

idene-diphenyl-dihydrotetrazene,  $\text{Ph}\cdot\text{CH}:\text{N}\cdot\text{NPh}$ , m.p.  $190^\circ$ , was obtained

from benzylidene-phenyl-hydrazone; other products are formed at the same time, among them benzylidene-benzoyl-diphenyl-dihydrotetrazene,  $\text{Ph}\cdot\text{CH}:\text{N}\cdot\text{NPh}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{Ph}$ , m.p.  $105\text{--}106^\circ$ ; the latter loses two hydrogen atoms and becomes benzoyl-formazyl-benzene,  $\text{Ph}\cdot\text{C}[:\text{N}\cdot\text{N}(\text{Ph})\text{COPh}]\text{N}:\text{NPh}$  (p. 312) (Busch, Ber. 49, 317, 2345). Other oxidising agents, e.g., air in alkaline solution, transform the aldehyde-hydrazones into osazones of diketones, e.g., benzaldehyde-hydrazone into benzilosazone. There is yet a third type of oxidation, leading to the so-called dehydra-benzal-phenylhydrazone,

$\text{Ph}\cdot\text{C}:\text{N}\cdot\text{NHPh}$ , m.p.  $207^\circ$  (Bamberger, Ber. 34, 528). Triphenyl-hydrazine

$\text{Ph}\cdot\text{N}\cdot\text{N}:\text{CHPh}$  reacts with lead dioxide at  $-60^\circ$  with the formation of the very unstable hexa-phenyl-tetrazane,  $\text{Ph}_2\text{N}\cdot\text{NPh}\cdot\text{N}:\text{Ph}_2$ , decomposing into two molecules of the blue, free triphenyl-hydrazyl,  $\text{Ph}_2\text{N}\cdot\text{NPh}\cdot$ , which will be discussed in the section on free radicals (Vol. IV) (Goldschmidt, Ber. 53, 44).

BUZYLENE or DIAZO-HYDRAZO-COMPOUNDS. Hippuryl-phenyl-buzylene,  $\text{PhN}=\text{N}\cdot\text{NH}\cdot\text{NHCO}\cdot\text{CH}_2\text{NHCOPh}$ , m.p.  $84^\circ$ , is a hippuric derivative of the unknown nitrogen hydride, buzylene,  $\text{NH}=\text{N}\cdot\text{NH}\cdot\text{NH}_2$ . It is produced from hippuryl-hydrazine and phenyl-diazonium sulphate (Curtius, Ber. 26, 1268). Diazobenzene-phenyl-hydrazide,  $\text{PhN}:\text{N}\cdot\text{NPh}\cdot\text{NH}_2$ , m.p.  $71^\circ$  (de-

comp.), is derived from the same nitrogen hydride. It has been prepared (1) by the action of a diazonium salt on phenylhydrazine (*Fischer*, Ber. 43, 3500), (2) by oxidising phenylhydrazine with iodine solution (*Stollé*, J. pr. 66, 336). The first method has been used for preparing a number of nuclear substituted derivatives and diazobenzene-alkyl-hydrazides. In the same way as the *as*-hydrazines are oxidised by potassium permanganate to tetrazenes (see above) diazophenyl-hydrazides are converted by oxidation into compounds containing a chain of 8 nitrogen atoms, called

**OCTAZENES.** *bis*-Diazobenzene-diphenyl-tetrazene, *tetraphenyl-octazene*,  $\text{PhN:N(Ph)N:N(Ph)N:NPh}$ , m.p. 51°; *bis*-bromodiazobenzene-diphenyl-tetrazene, m.p. 60°. These substances decompose readily and are explosive (*Wohl*, Ber. 33, 2741).

#### 4. AROMATIC COMPOUNDS OF PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH, BORON, AND SILICON. (Cf. Vol. I)

The phenyl derivatives of phosphorus, arsenic, antimony, bismuth, boron, and silicon, are similar in type to the aromatic nitrogen compounds. They are best prepared from the chlorides of the various elements which react (1) with benzene at a red heat, HCl being eliminated; (2) with benzene and aluminium chloride; (3) with diphenyl mercury; (4) with phenyl magnesium bromide (*Pfeiffer*, Ber. 37, 4620); (5) with sodium and phenyl chloride or bromide. Further methods are (6) the action of alloys consisting of the element in question and an alkali metal, on aryl halides; (7) the action of aralkyl-chloro-compounds, or aryl chlorides on the halides of the elements in the presence of an equivalent quantity of an alkali metal (Ger. Pat. 508,667).

Special importance attaches to certain aromatic arsenic compounds, which kill trypanosomes, but are comparatively feebly toxic to man, and are therefore of the highest value as medicines in protozoic diseases. It has been found that compounds which correspond to cacodylic acid (Vol. I, p. 211) and contain pentavalent arsenic are less effective than those containing trivalent arsenic (*Ehrlich*, Ber. 42, 17). The mono-sodium salt of *p*-amino-phenylarsinic acid (p. 168) is used under the name of *atoxyl* for combating sleeping sickness, and diamino-dihydroxy-arsenobenzene (p. 168), known as *salvarsan* (originally "Ehrlich 606") for the treatment of syphilis. A number of derivatives of these two substances which are of therapeutic value have been prepared, *e.g.*, *arsacetin*, *neosalvarsan*, *etc.*

**PHENYL-PHOSPHORUS COMPOUNDS.** *Michaelis* succeeded, in 1876, in overcoming the experimental difficulties of attaching the phenyl residue to phosphorus, and in preparing phosphenyl chloride, which then became the starting material for the preparation of other phosphenyl compounds. Some phosphenyl compounds correspond in composition to aromatic nitrogen derivatives and have been named accordingly:

|                                                           |                                                                 |
|-----------------------------------------------------------|-----------------------------------------------------------------|
| Aniline, $\text{C}_6\text{H}_5\text{NH}_2$                | $\text{C}_6\text{H}_5\text{PH}_2$ , phenyl-phosphine            |
| Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$           | $\text{C}_6\text{H}_5\text{PO}_2$ , phosphino-benzene           |
| Azobenzene, $\text{C}_6\text{H}_5\text{N:NC}_6\text{H}_5$ | $\text{C}_6\text{H}_5\text{P:PC}_6\text{H}_5$ , phosphobenzene. |

Phenylphosphine, *phosphaniline*,  $\text{C}_6\text{H}_5\text{PH}_2$ , b.p. 160°, is obtained from phosphenyl chloride by treatment with hydrogen iodide, and then with alcohol. It is a liquid with an extremely disagreeable smell. On standing in the air it is oxidised to phosphenyl oxide,  $\text{C}_6\text{H}_5\cdot\text{PH}_2\text{O}$ , a crystalline mass, soluble in water. Phenyl-phosphine combines with hydrogen iodide to form phenyl-phosphonium iodide,  $\text{C}_6\text{H}_5\cdot\text{PH}_2\text{I}$ , from which water regenerates phenylphosphine. Aryl-dialkyl-phosphines are obtained by the action of two mols. of alkyl magnesium halides on aryl-phosphine dichlorides (see below) (*Jackson*, J. 1930, 2298). Phenyl-dimethyl-phosphine,  $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$ , b.p. 83–84° (13.5 mm.), and phenyl-diethyl-phosphine, b.p. (10 mm.) 96–98° (*Meisenheimer*, Ann. 449, 227).

*p*-Xylyl-dimethyl-phosphine, b.p. (12 mm.) 106°, changes into the phosphine oxide, m.p. 94–95°, on boiling in a current of air. Addition product with mercuric chloride, m.p. 225°; with methyl iodide, m.p. 204°. Xylyl-diethyl-phosphine, b.p. (52 mm.) 157°. Both these phosphines have a penetrating odour of hyacinth (*Jackson*, J. 1931, 575).

Phosphenyl chloride,  $\text{C}_6\text{H}_5\text{PCl}_2$ , b.p. 225°;  $d_{20}^{20}$  1.319, is a liquid of high refractive power, which fumes in air. It is formed (1) when benzene and phosphorus

trichloride are passed through a red-hot tube (*Bowles*, *Am.* 51, 1406); (2) by heating diphenyl mercury with phosphorus trichloride; (3) by heating benzene and phosphorus trichloride with aluminum chloride. The last reaction has been used to introduce the chlorophosphine residue into *dimethylaniline* and *phenyl-alkyl ethers*. Phosphenyl chloride combines with chlorine to give **phosphenyl tetrachloride**,  $C_6H_5 \cdot PCl_4$ , m.p.  $73^\circ$ , with oxygen to give **phosphenyl oxychloride**,  $C_6H_5 \cdot PCl_3O$ , b.p.  $258^\circ$ , and with sulphur to give **phosphenyl thiochloride**, b.p. (130 mm.)  $205^\circ$ . With water, phosphenyl chloride forms **phosphenylous**, or **phenyl-hypophosphorous acid**,  $C_6H_5 \cdot PHO \cdot OH$ , m.p.  $70^\circ$ , and **phosphenyl tetrachloride** yields **phosphenylic**, or **phenyl-phosphinic acid**,  $C_6H_5 \cdot PO(OH)_2$ , m.p.  $150^\circ$  (*Nijk*, *Rec.* 41, 461). *p*-Tolyl-phosphoro-chloride,  $CH_3[4]C_6H_4[1]PCl_2$ , forms a tetrachloride, which gives **tolyl-trianilino-phosphonium chloride**,  $CH_3[4]C_6H_4 \cdot P[1](NHPh)_3Cl$ , m.p.  $245^\circ$ , with aniline, and this with sodium hydroxide gives the hydroxide,  $CH_3C_6H_4 \cdot P(NHPh)_3OH$ , m.p.  $240^\circ$ .

**Phosphino-benzene**, *phenyl-phosphinic anhydride*,  $C_6H_5PO_2$ , m.p.  $100^\circ$ , is obtained from phosphenyl oxychloride and phenyl-phosphinic acid. **Phospho-benzene**,  $C_6H_5P \cdot PCl_2$ , m.p.  $150^\circ$ , is obtained from phosphenyl chloride and phenyl-phosphine (*Michaelis*, *Ber.* 10, 812; 25, 1747).

**Diphenyl-phosphine chloride**,  $(C_6H_5)_2PCl$ , b.p.  $179-180^\circ$  (16 mm.), is obtained by heating phosphenyl chloride alone at  $280^\circ$ , or with mercury diphenyl at  $220^\circ$  (*Dörken*, *Ber.* 21, 1505). It gives with phenol, **phenoxy-diphenyl-phosphine**,  $(C_6H_5)_2POC_6H_5$ , b.p. (62 mm.)  $265-270^\circ$  (*Michaelis*, *Ber.* 18, 2118), and with dilute sodium hydroxide, **diphenyl-phosphine**,  $(C_6H_5)_2PH$ , b.p.  $280^\circ$ , and **diphenyl-phosphinic acid**,  $(C_6H_5)_2POOH$ , m.p.  $190^\circ$  (*Michaelis*, *Ber.* 15, 801).

**Triphenyl-phosphine**,  $(C_6H_5)_3P$ , m.p.  $79.5^\circ$ , b.p. approx.  $360^\circ$ ,  $\mu$  1.45, has been obtained from bromobenzene by the action of phosphenyl chloride, or phosphorus trichloride and sodium, and also by the action of phosphorus trichloride on phenyl magnesium bromide (*Pfeiffer*, *Ber.* 37, 4621). It combines with alkyl halides to give quaternary phosphonium salts, with phenyl magnesium bromide to give **tetraphenyl-phosphine bromide**,  $(C_6H_5)_4PBr$ , m.p.  $287^\circ$  (*Dodonov*, *Ber.* 61, 907), and with  $\alpha$ -halogeno-ketones, such as monochloroacetone,  $CH_3COCH_2Cl$ , to give compounds which readily change to the so-called *phosphoro-keto-betaines*, e.g.,

$(C_6H_5)_3P \begin{array}{c} \diagup CH_2 \\ \diagdown O \end{array} \begin{array}{c} \diagup OH \\ \diagdown CH_3 \end{array}$  (?) (*Michaelis*, *Ber.* 32, 1566). It also combines with

bromine to give **triphenyl-phosphine dibromide**,  $(C_6H_5)_3PBr_2$ , which is converted into **triphenyl-phosphine dihydroxide**,  $(C_6H_5)_3P(OH)_2$ , when boiled with aqueous sodium hydroxide. When heated to  $100^\circ$ , the latter is converted into **triphenyl-phosphine oxide**,  $(C_6H_5)_3PO$ , m.p.  $156^\circ$ , b.p. above  $360^\circ$ . The same compound is obtained by the action of phosphorus oxychloride on phenyl magnesium bromide (*Sauvage*, *C.r.* 139, 674), and can be converted into the **dichloride**,  $(C_6H_5)_3PCl_2$ , m.p.  $176^\circ$ , by the action of phosphorus pentachloride. With Grignard reagents, the dichloride gives magnesium-halogeno-derivatives, which react with aliphatic alcohols giving derivatives of pentavalent phosphorus of the general formula  $Ar_3PAlk_2$ : **triphenyl-dimethyl-phosphine**, m.p.  $163-166^\circ$ , **triphenyl-diethyl-phosphine**, m.p.  $172^\circ$ , **triphenyl-di-n-propyl-phosphine**, m.p.  $179-182^\circ$ . For condensation products of triaryl-phosphines and phenols, see *Grignard*, *C.r.* 192, 592.

**Triphenyl-phosphine oxide**,  $Ph_3PO$ , is isomeric with **phenoxy-diphenyl-phosphine**,  $(C_6H_5)_2POC_6H_5$  (*q.v.*). The vapour density of both these compounds, determined at reduced pressure, indicates the single molecular formula (*Vol.* 1, p. 13). It follows that phosphorus must be pentavalent in the former, and trivalent in the latter compound (*Michaelis*, *La Coste*, *Ber.* 18, 2118). Chlorine attached to the trivalent phosphorus behaves differently from the chlorine atoms attached to the fourth and fifth valencies in pentavalent phosphorus. The equivalence of the five valencies of phosphorus has been investigated by *Anschütz*, *Ann.* 482, 25, and *Grignard*, *C.r.* 192, 592.

**Triphenyl-phosphine sulphide**,  $(C_6H_5)_3PS$ , m.p.  $161^\circ$ , is obtained from phosphorus oxy sulphide and phenyl magnesium bromide. For other sulphur compounds of phenyl-phosphines see *Strecker*, *Ber.* 49, 63.

**PHENYL-ARSENIC COMPOUNDS.** (See *P. Ehrlich* and *S. Hata*, *Die experimentelle Chemotherapie der Spirillosen*, Berlin, 1910; *G. W. Raiziss* and *J. L. Gawron*, *Organic Arsenical Compounds*, New York, 1923.)



The following compounds have been prepared by methods similar to those used in the preparation of phenyl derivatives of phosphorus trichloride: **Phenylarsine dichloride**,  $C_6H_5AsCl_2$ , b.p. (14 mm.)  $114^\circ$ . **Diphenylarsine chloride**,  $(C_6H_5)_2AsCl$ , dimorphous, m.p.  $18.3^\circ$  and  $38.8^\circ$ ; **diphenylarsine cyanide**,  $(C_6H_5)_2AsCN$ , m.p.  $31^\circ$  (the last two compounds are used in gas warfare under the name "Blaukreuz" (blue cross)). **Diphenylarsine iodide**,  $(C_6H_5)_2AsI$ , m.p.  $41-42^\circ$ . **Triphenylarsine**,  $(C_6H_5)_3As$ , m.p.  $58^\circ$ , dipole moment 1.07. **Phenylarsine oxide**, m.p.  $142-145^\circ$ , is obtained from phenylarsonic acid (see below) by the action of sulphur dioxide; a polymer is formed at the same time, m.p.  $210-220^\circ$  (Steinkopf, J. pr. 141, 301). **Phenylarsine sulphide**,  $C_6H_5AsS$ . **Phenylarsonic acid**,  $C_6H_5AsO(OH)_2$ . **Diphenylarsonic acid**,  $(C_6H_5)_2AsOOH$ . **Arseno-benzene**,  $C_6H_5As:AsC_6H_5$  (Michaelis, Ann. 201, 191; 207, 195; 270, 139; 321, 141; Ber. 27, 263. Philips, Ber. 19, 1031. Holle, Ber. 25, 1521. Benda, Ber. 41, 2367. Kamai, Ber. 68, 1893. Sturmioli, Boll. Farm. 1920, Morgan, J. 117, 777. Burrow, J. 117, 1373; Pope, J. 117, 1447. Everett, J. 1930, 1691. Kennedy, J. 1932, 2781. Blicke, Am. 52, 2946. Champetier, Bull. 47, 1131. Brit. Pat. 309,249).

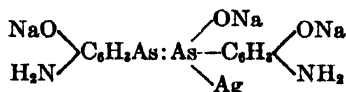
**p-Aminophenylarsonic acid**, **arsanilic acid**,  $NH_2 \cdot C_6H_4AsO(OH)_2$ , lustrous white needles, m.p. above  $200^\circ$ , is formed, together with **p,p'-diaminodiphenylarsonic acid**,  $(NH_2C_6H_4)_2AsOOH$ , m.p.  $232^\circ$ , by heating aniline arsenate to  $190-200^\circ$  (Benda, Ber. 41, 2367; Kazimierzczuk, Arch. Ch. Farm. 3, 30). **Arsanilic acid** is reduced by hydrogen iodide or sulphur dioxide to **p-aminophenylarsine oxide**,  $NH_2C_6H_4AsO \cdot 2H_2O$ , but by tin and hydrochloric acid to the yellow **p,p'-diamino-arsenobenzene**,  $NH_2C_6H_4As:AsC_6H_4NH_2$ , m.p.  $140^\circ$  (Ger. Pat. 206,344). For the relation between the nature and position of substituents and the therapeutic and toxic properties of phenyl-arsonic acids, see Fournéau, Ann. Inst. Pasteur, 1923. In most cases the toxicity of the *p*-arsanilic acids is reduced by N-acetylation, and increased by N-alkylation. Among the derivatives of **arsanilic acid** which are of value on account of their trypanocidal or spirillicidal action, the following may be mentioned: **tryparsamide**, the mono-sodium salt of amino-acet-

**amino-phenyl-arsinic acid**,  $NaO \begin{array}{c} \diagup \\ HO \end{array} As \cdot OC_6H_4 \cdot NH \cdot CH_2CONH_2$ , obtained by the action of chloro-acetamide on atoxyl; **arsacetin**, the sodium salt of N-acetyl-ars-

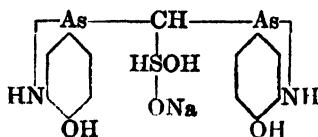
**anilic acid**,  $NaO \begin{array}{c} \diagup \\ HO \end{array} As \cdot O \cdot C_6H_4 \cdot NH \cdot COCH_3$ , obtained by acetylating atoxyl;

**stovarsol** ("Fournéau 270"),  $NaO \begin{array}{c} \diagup \\ HO \end{array} As \cdot O \cdot C_6H_3(OH) \cdot NH \cdot COCH_3$ , the sodium salt of *o*-hydroxy-*p*-acetamino-phenylarsonic acid.

**p-Hydroxy-phenylarsonic acid**,  $HO \cdot C_6H_4AsO(OH)_2$ , can be obtained from **arsanilic acid** *via* its diazo-compound. The compound melts at  $174^\circ$ . It can also be obtained by heating phenol with arsenic acid (Ger. Pat. 205,616). By nitration and reduction this compound yields first, **m-amino-p-hydroxyphenylarsonic acid**,  $HO(NH_2)C_6H_4AsO(OH)_2$ , then **m,m'-diamino-p,p'-dihydroxyarsenobenzene**,  $HO(NH_2)C_6H_4As:AsC_6H_3(NH_2)OH$ , of which the dihydrochloride is known as **salvarsan**. Successive treatment of **salvarsan** with a silver salt and alkali gives **silver-salvarsan**, a substance of considerable therapeutic value, of the formula:



**Neosalvarsan** is a condensation product of **salvarsan** and sodium formaldehyde sulphonylate, and apparently has the formula:



(*Lasch*, *Klin. Wochenschr.* 1929). For homologous aminophenylarsonic acids and their reaction products, see *Kahn*, *Ber.* 41, 3859. For azo-dyes containing arsenic, obtained from *p*-nitroso-phenylarsonic acid and toluylene diamine by means of hydroxylamine hydrochloride see *Karrer*, *Ber.* 45, 2359.

**PHENYL-ANTIMONY COMPOUNDS.** Triphenyl-stibine,  $(C_6H_5)_3Sb$ , m.p. 48°, dipole moment 0.57, was first prepared by *Michaelis* (*Ann.* 233, 43) by adding sodium to a benzene solution of chlorobenzene and antimony trichloride, and later by *Pfeiffer* by the action of phenyl magnesium bromide on antimony trichloride (*Ber.* 37, 4621). When heated with antimony trichloride in xylene it gives phenyl-stibine dichloride, m.p. 58°, b.p. 290°, from which the oxide, sulphide, tetrachloride, and phenyl-stibinic acid,  $[C_6H_5SbO(OH)_2] \cdot H_2O$ , have been prepared (*Hasenbaumer*, *Ber.* 31, 2910; *Schmidt*, *Ann.* 421, 174). When phenyl-stibine oxide is heated to 90° in a current of nitrogen, and subsequently treated with acetic acid, diphenyl-stibine acetate,  $(C_6H_5)_2Sb \cdot OCOCH_3$ , m.p. 133–135° is obtained, which has been further converted into the chloride, bromide, iodide, and cyanide, m.p. 68°, 86°, 68–70°, and 115–116°, respectively (*Steinkopf*, *Ber.* 65, 409; *Blüke*, *Am.* 53, 1025). Triphenyl-stibine dichloride, m.p. 142°, is obtained from triphenyl-stibine and chloride. Triphenyl-stibine sulphide,  $Ph_3SbS$ , m.p. 120° is obtained by the action of alcoholic ammonium sulphide on triphenyl-stibine dibromide (*Kaufmann*, *Ber.* 41, 2762). For the anaesthetic and trypanocidal effect of phenyl-stibine compounds, see *Balaban*, *J.* 1930, 1685; *Nyogy*, *Indian Soc.* 8, 56.

**PHENYL-BISMUTH COMPOUNDS.** Bismuth triphenyl,  $(C_6H_5)_3Bi$ , m.p. 78°, dipole moment zero, is obtained from the alloy of bismuth and sodium and bromobenzene, or by the action of phenyl magnesium bromide on bismuth trichloride (*Michaelis*, *Ann.* 251, 324; *Pfeiffer*, *Ber.* 37, 4622; *Supniewski*, *Am.* 48, 507). Diphenyl-bismuth iodide,  $(C_6H_5)_2BiI$ , m.p. 133° (*Gillmeister*, *Ber.* 30, 2843).

**PHENYL-BORON COMPOUNDS.** By the action of mercury diphenyl or organo-magnesium halides (*Ger. Pat.* 371,467) on boron trichloride, phenyl-boron dichloride,  $PhBCl_2$ , m.p. 0°, b.p. 175°, and diphenyl-boron chloride,  $Ph_2BCl$ , b.p. 271°, are obtained. Phenyl-boron dibromide,  $PhBBr_2$ , m.p. 33°, b.p. (20 mm.) 100°. Diphenyl-boron bromide,  $Ph_2BBr$ , m.p. 25° (*Michaelis*, *Ber.* 27, 224; *Ann.* 315, 29). Phenylboric acid,  $PhB(OH)_2$ , m.p. 221°, is obtained by the action of phenyl magnesium bromide on methyl borate, or by the action of water on phenyl-boron dichloride. On heating it gives phenyl-boron oxide,  $PhBO$  (*Krause*, *Ber.* 55, 1262). *o*-, *m*-, and *p*-Nitrophenylboric acids, m.p. 147.5°, 319°, and above 360°, respectively (*Seaman*, *Am.* 53, 711).

Triphenyl-boron,  $Ph_3B$ , m.p. 136°, b.p. (15 mm.) 203°, obtained by the action of boron trifluoride on phenyl magnesium bromide (*Krause*, *Ber.* 55, 1262), gives with Na or Na-amalgam sodio-triphenyl-boryl,  $Ph_3BNa$ , and analogous compounds with Li, K, Rb, Cs (*Krause*, *Ber.* 59, 777). Other aromatic compounds of tetravalent boron are described in the section on free radicals, Vol. IV.

**PHENYL-SILICON COMPOUNDS** were first discovered by *Ladenburg* in 1874, but most of our knowledge of these compounds is due to *F. S. Kipping* (*J.* 1899–1935). Phenyl-silicon trichloride,  $PhSiCl_3$ , b.p. 197° is prepared by the action of silicon tetrachloride on mercury diphenyl (*Ladenburg*, *Ann.* 173, 151) or phenyl magnesium bromide. With water it gives silico-benzoic acid,  $PhSiO_2OH$ , m.p. 92°, and with ethyl alcohol, orthosilico-benzoic ester,  $PhSi(OEt)_2$ , b.p. 173°, which can also be obtained from orthosilicic ester and phenyl magnesium bromide (*Khotinsky*, *Ber.* 41, 2946). Phenyl-triethyl-silicane,  $PhSiEt_3$ , a liquid boiling at 230°, is produced by the action of zinc diethyl on phenyl-silicon trichloride. Triphenyl-methyl-silicane,  $Ph_3SiMe$ , m.p. 67°, and triphenyl-ethyl-silicane,  $Ph_3SiEt$ , m.p. 76°, are obtained from triphenyl-silicon-chloride,  $Ph_3SiCl$ , m.p. 111°, by the action of methyl- and ethyl-magnesium iodide, respectively. Mixed compounds with four different radicals, e.g., phenyl-methyl-ethyl-propyl-silicane,  $PhSiMeEtPr$ , a liquid, b.p. 231°, have been prepared by treating silicon tetrachloride successively with phenyl-, methyl-, ethyl-, and propyl-magnesium bromide. For optical activity of organo-silicon compounds see *Kipping*, *et al.*, *J.* 97, 755.

Triphenyl-silicane,  $Ph_3SiH$ , m.p. 203° (*Ladenburg*, *Ber.* 40, 2278). Silicon tetraphenyl,  $Ph_4Si$ , m.p. 228°, b.p. above 300°, has been obtained by acting on an ethereal solution of silicon tetrachloride and chlorobenzene with sodium (*Polis*,

Ber. 19, 1012). When heated with bromine it gives triphenyl-silicon bromide,  $\text{Ph}_3\text{SiMgBr}$ , m.p.  $120^\circ$ ; this latter, when boiled with potassium carbonate solution, is converted into triphenyl-silicol,  $\text{Ph}_3\text{SiOH}$ , m.p.  $155^\circ$ . Diphenyl-silicol,  $\text{Ph}_2\text{Si}(\text{OH})_2$ , m.p.  $139^\circ$ , is converted on melting into trimolecular diphenyl-silicone,  $(\text{Ph}_2\text{SiO})_3$ , m.p.  $110^\circ$  (Dillthey, Ber. 37, 1139).

Mixed aliphatic-aromatic tetra-alkyl-silicon derivatives like ethyl-propyl-dibenzyl-silico-monosulphonic acid,  $\text{PrEt}(\text{PhCH}_2)\text{Si}(\text{CH}_2\text{C}_6\text{H}_5\text{SO}_3\text{H})$ , have been resolved into optical isomers.

The compounds  $\text{Si}_4\text{Ar}_3$  and those of trivalent silicon are described in the section on free radicals, Vol. IV.

## 5. PHENYL METALLIC DERIVATIVES\*

The phenyl and other aryl groups have been combined with many metals, such as Li, Na, K, Mg, Zn, Hg, Al, Cr, Th, Ge, Sn, Ag, Au, and Pb. A number of these compounds, e.g., those of tetravalent chromium, and trivalent tin and lead, are to be regarded as free radicals (Vol. IV).

Phenyl-lithium,  $\text{PhLi}$ , is known only in solution, which is obtained by the action of lithium on bromo- or iodo-benzene. When treated with carbon dioxide it gives only a small amount of lithium benzoate, but it has, in general, the properties of a Grignard reagent.

Phenyl-sodium,  $\text{PhNa}$ , is a spontaneously inflammable brown powder, which is obtained by the action of an excess of sodium on mercury diphenyl. It is probably an intermediate product in Fittig's reaction between sodium and bromobenzene (Acree, Am. 29, 588).

Triphenylmethyl-sodium,  $\text{Ph}_3\text{CNa}$ , is a brick-red substance, which reacts violently with the oxygen of the air. It is obtained by the action of sodium on triphenylmethyl (*q.v.*) (Schlenk, Ber. 49, 608; Ann. 464, 1).

**PHENYL-POTASSIUM COMPOUNDS.** Potassium compounds of the general formula,  $\text{Alk} \cdot \text{Ar}_2\text{C} \cdot \text{K}$ , are obtained when an ether solution of the ethers of alkyl-diphenyl-carbinols,  $\text{Alk} \cdot \text{Ar}_2\text{C} \cdot \text{OR}$ , is acted upon by the metal. Ethyl-diphenyl-methyl-potassium, an orange powder, gives  $\alpha, \alpha$ -diphenylpropionic acid with carbon dioxide. This, and other similar potassium and sodium compounds will add on to unsaturated hydrocarbons (Ziegler, Ann. 437, 227; 473, 1; Ber. 61, 253).

Magnesium-diphenyl,  $\text{Ph}_2\text{Mg}$ , is a light, pale-yellow powder, which dissolves readily in a mixture of benzene and ether. It is obtained by heating mercury-diphenyl with magnesium powder and a little ethyl acetate to  $180$ – $185^\circ$  (Waga, Ann. 282, 320; Gilman, Rec. 49, 202). It inflames in air, and reacts violently with water, forming  $\text{Mg}(\text{OH})_2$  and benzene.

**ARYL MAGNESIUM HALIDES.**† Phenyl magnesium bromide and iodide,  $\text{PhMgBr}$  and  $\text{PhMgI}$ , and homologous aryl-magnesium halides are formed in a similar manner to the alkyl-magnesium halides (Vol. I, p. 219), by the action of magnesium on ether solutions of bromo- and iodo-benzene. They are, like the alkyl compounds, exceedingly useful in syntheses. 1. They combine with carbon dioxide to give salts of aromatic carboxylic acids, such as benzoic acid,  $\text{PhCOOH}$ . 2. With carbon oxysulphide,  $\text{COS}$ , thiocarboxylic acids, e.g.,  $\text{PhCOSH}$ , and triphenyl-carbinols, e.g.,  $\text{Ph}_3\text{COH}$ , are formed. 3. With carbon disulphide, carbithionic acids, e.g.,  $\text{PhCSSH}$ , are formed. 4. Triphenyl-carbinol is obtained by the action of phosgene and ethyl benzoate on  $\text{PhMgBr}$ . 5. Thioanilides, e.g.,  $\text{CH}_3\text{CSNHPh}$ , are formed with mustard oils. 6. Alkyl-aldehyde-imines, e.g.,  $\text{PhCH}=\text{NMe}$ , are formed with isocyanides. 7. Diazoaminobenzene,  $\text{PhN}_2\text{NHPh}$ , is formed with phenyl azide. 8. With nitrosyl chloride  $\text{PhMgBr}$  gives nitroso-benzene. 9. With oxygen, phenol and phenyl-methyl-carbinol are formed, the ether employed as solvent participating in the formation of the latter. 10. Sulphur and selenium produce thiophenols and seleno-phenols,  $\text{PhSH}$  and  $\text{PhSeH}$ . 11. Iodine gives iodobenzene and  $\text{MgBrI}$ . 12. Primary, secondary, and tertiary aromatic alcohols are formed with formaldehyde and other

\* See J. Schmidt, *Organometalloverbindungen*, Stuttgart, 1934; a survey of the more recent literature is given by Hofmann, Ber. 65, A 30.

† See Runge, *Organomagnesiumverbindungen*, Stuttgart, 1932.

aldehydes, ketones, and esters. 13.  $\text{PhMgBr}$  and an excess of ethyl formate gives benzaldehyde, while acetonitrile or acetamide give acetophenone.

For the preparation of magnesium compounds without the use of ether see *Schorigin*, Ber. 66, 1426.

Zinc diphenyl,  $\text{Ph}_2\text{Zn}$ , m.p.  $104^\circ$ , is obtained by the action of zinc wool on mercury diphenyl in boiling xylene. The *p*-halogen substituted compounds are obtained similarly. Zinc di-*o*-tolyl, m.p.  $207-213^\circ$ .

Mercury diphenyl,  $\text{Ph}_2\text{Hg}$ , m.p.  $125^\circ$ , was first obtained by *Otto* and *Dreher* (Ann. 154, 93) by treating a solution of bromobenzene in benzene with liquid sodium amalgam; the reaction is accelerated by the addition of ethyl acetate. It can also be obtained by the action of  $\text{HgCl}_2$  or  $\text{HgCl}$  on  $\text{PhMgBr}$  (*Pfeiffer*, Ber. 37, 1127), and from aryl-diazonium mercury halides,  $\text{Ar}\cdot\text{N}_2\cdot\text{HgCl}_2$ , in acetone, by the action of Cu powder (*Nesmejanov*, Ber. 62, 1019). Details of preparation are given by *Hein*, Ber. 58, 1499, *Gilman*, Am. 51, 928, *Borgstrom*, *ibid.*, 3387, and *Calvery*, Org. Synth. 9, 54. It crystallises in colourless, rhombic prisms, and can be sublimed. It turns yellow when exposed to light. It dissolves readily in benzene and carbon disulphide, more sparingly in alcohol and ether, and is insoluble in water. When distilled it breaks up almost completely into diphenyl, benzene, and mercury. By the action of sodium on mercury diphenyl in benzene solution, the highly reactive sodium phenyl,  $\text{PhNa}$ , is formed. Acids decompose it with the formation of benzene and mercury salts. It is the starting material for the preparation of many phenyl-metallic compounds and "pseudo"-metallic compounds. *Kekulé* and *Franchmont* prepared triphenylmethane (p. 525) from mercury diphenyl and benzal chloride. Halides are formed with the halogens: mercury phenyl chloride,  $\text{PhHgCl}$ , m.p.  $250^\circ$ , mercury phenyl bromide,  $\text{PhHgBr}$ , m.p.  $267^\circ$ , mercury phenyl iodide,  $\text{PhHgI}$ , m.p.  $265^\circ$ . Mercury phenyl hydroxide  $\text{PhHgOH}$ , is prepared from the chloride by the action of silver oxide in alcohol. Di-*p*-tolyl mercury, m.p.  $243^\circ$  (*Nesmejanov*, Ber. 62, 1019). Di-*p*-anisyl mercury, m.p.  $198-200^\circ$  (*Blicke*, Am. 51, 3479).

Mercury phenyl acetate,  $\text{PhHgOCOCH}_3$ , is formed directly when benzene and mercuric acetate are heated to  $110-120^\circ$ , and by boiling mercuric oxide and benzene with glacial acetic acid (Br. Pat. 325,846; *Nesmejanov*, Ber. 66, 199). By similar methods it is possible to introduce a mercury atom in place of a nuclear hydrogen atom in many aromatic compounds, such as nitrobenzenes, anilines, phenols, benzoic acid, etc. Indeed it has become customary to speak of the mercuration of aromatic compounds in the same way as one speaks of chlorination, nitration, and sulphonation, as a general reaction. In these compounds the mercury is fairly firmly attached to the nucleus. By energetic methods even more than one hydrogen atom can be replaced, and compounds such as  $\text{C}_6\text{H}_4(\text{HgOCOCH}_3)_2$ ,  $\text{C}_6\text{H}_3(\text{HgOCOCH}_3)_3$  and  $\text{C}_6\text{H}_2(\text{HgOCOCH}_3)_4$ , are produced (*Acree*, Am. 29, 588).

MERCURY-DIARYLS, see *Ladenburg*, Ann. 173, 162; *Jacobsen*, Ber. 14, 2112; 17, 2374; 22, 1220; *Weller*, Ber. 20, 1719, etc.

PHENYL-ALUMINIUM COMPOUNDS. Triphenylaluminium,  $\text{Ph}_3\text{Al}$ , m.p.  $196-200^\circ$ , is obtained from aluminium and mercury diphenyl. It is a powder which is readily attacked even by dry air. It inflames with water, giving benzene, diphenyl, and aluminium oxide. It combines with alkali metals (*Hilpert*, Ber. 45, 2828; *Krause*, Ber. 59, 1428). Tri-*p*-tolylaluminium is obtained from aluminium and di-*p*-tolyl-mercury (*Krause*, Ber. 63, 2401).

PHENYL-CHROMIUM COMPOUNDS were discovered by *Hein*. Several series of aryl-compounds derived from 6-, 5-, 4-, and 3-valent chromium are known. Pentaphenyl-chromium bromide,  $\text{Ph}_5\text{CrBr}$ , is an orange-red, amorphous powder, which is prepared by the action of  $\text{CrCl}_3$  on  $\text{PhMgBr}$ . It is converted by alcoholic potash into pentaphenyl-chromium hydroxide,  $\text{Ph}_5\text{CrOH}\cdot 4\text{H}_2\text{O}$ , in which part of the water is water of constitution (*Hein*, Ber. 52, 195; 54, 1905). This gives, with hydrogen halides, tetraphenyl-chromium bromide and iodide, both crystallising with chloroform of crystallisation, the former melting at  $138^\circ$ , and the latter, when freed from chloroform, at  $178^\circ$  (*Hein*, Ber. 54, 2708, 2727). Tetraphenyl-chromium hydroxide,  $\text{Ph}_4\text{CrOH}$ , forms orange crystals, m.p.  $104-105^\circ$ . It is formed from the above halides by the action of silver oxide, or electrolytically (*Hein*, Ber. 57, 8). Tetraphenyl-chromium,  $(\text{Ph}_4\text{Cr})_n$ , forms orange-red or copper-red crystals, and is obtained by electrolysis of  $\text{Ph}_4\text{CrI}$  (*Hein*, Ber. 59, 362). Triphenyl-chromium iodide,  $\text{Ph}_3\text{CrI}$ , m.p.  $67^\circ$ . Triphenyl-chromium

**hydroxide**,  $\text{Ph}_2\text{CrOH}$ , is a base which gives an aqueous solution as strong as  $\text{NaOH}$ . **Triphenyl-chromium**,  $\text{Ph}_3\text{Cr}$  is obtained from the iodide by electrolysis (*Hein*, Ber. 61, 2255).

**PHENYL-THALLIUM COMPOUNDS.** Thallium halides,  $\text{THal}$ , react with phenylboric acid (p. 169) with the formation of phenyl-thallium dihalides or diphenyl-thallium monohalides, depending on the proportions of the reactants employed. **Phenyl-thallium dichloride**, and **dibromide**, m.p.  $235^\circ$  and  $152^\circ$  (decomp.), respectively. **Diphenyl-thallium chloride**, and **bromide**, both melt above  $320^\circ$ . Diaryl- (phenyl, *o*- and *p*-tolyl) thallium halides have also been prepared from aryl magnesium bromides and thallium halides. On hydrolysis the monohalides give the oxides  $(\text{Ar}_2\text{Tl})_2\text{O}$ . The dihalides are decomposed by boiling water into diphenyl-thallium monohalides and thallium halides (*God-dard*, J. 121, 36, 256, 482; *Challenger*, J. 1931, 1462). **Triphenyl-thallium**, m.p.  $188$ – $189^\circ$ , decomp. at  $215$ – $216^\circ$ , is obtained from  $\text{Ph}_2\text{TlBr}$  and  $\text{PhLi}$  (*Birch*, J. 1934, 1132).

**PHENYL-GERMANIUM COMPOUNDS.** **Tetraphenyl-germanium**,  $\text{Ph}_4\text{Ge}$ , m.p.  $236^\circ$ , is obtained from germanium bromide,  $\text{GeBr}_4$ , and  $\text{PhMgBr}$  in the presence of zinc chloride, or from germanium chloride,  $\text{GeCl}_4$ ,  $\text{PhBr}$  and  $\text{Na}$ . **Hexaphenyl-germano-ethane**,  $\text{Ph}_3\text{Ge}\cdot\text{GePh}_3$ , is formed at the same time, m.p.  $336^\circ$ . The former compound gives with halogens, **triphenyl-germanium bromide**,  $\text{Ph}_3\text{GeBr}$ , m.p.  $139^\circ$ , **fluoride**, m.p.  $77^\circ$ , **chloride**, m.p.  $116^\circ$ , **iodide**, m.p.  $157^\circ$ . By hydrolysis of the bromide with  $\text{NH}_3$  the **oxide**,  $(\text{Ph}_3\text{Ge})_2\text{O}$ , m.p.  $183$ – $184^\circ$  is formed (*Morgan*, J. 127, 1760; *Gibson*, J. 1929, 2759; *Kraus*, Am. 49, 457; 54, 1522; *Ordoff*, Am. 49, 2512; *Bauer*, Ber. 66, 1156 [ $\text{PhGe}$ -trihalides]; 67, 1041). The **sulphide**,  $(\text{Ph}_3\text{Ge})_2\text{S}$ , melts at  $138^\circ$  (*Burschkies*, Ber. 69, 1143). For the optically active phenyl-ethyl-isopropyl-germanium cation see *Schwarz*, Ber. 64, 2352.

**PHENYL-TIN COMPOUNDS.** By treating stannous and stannic chlorides with mercury diphenyl *Aronheim* (Ann. 194, 145) obtained **diphenyl-dichloro-stannane**, tin-diphenyl-dichloride,  $\text{Ph}_2\text{SnCl}_2$ , m.p.  $42^\circ$ . It can also be obtained by heating equivalent amounts of stannic chloride and tin-tetraphenyl at  $220^\circ$  in a sealed tube. With 3 mols. of stannic chloride and one of tin-tetraphenyl **phenyl-trichloro-stannane**, b.p.  $142$ – $143^\circ$  (25 mm.) is formed. With  $\text{HBr}$  and  $\text{HI}$  this gives **phenyl-tribromostannane**, b.p. (25 mm.)  $182$ – $183^\circ$  and **phenyl-iodostannane**, an unstable oil, respectively (*Waga*, Ann. 282, 328; *Kozeshkov*, Ber. 66, 996). **Diphenyl-stannane oxide**,  $\text{Ph}_2\text{SnO}$ , a white powder, and **phenyl-stannonic acid**,  $\text{PhSnO}\cdot\text{OH}$ , are formed from the hydrolysis of the dichloride. **Triphenyl-stannane chloride**, **bromide**, and **iodide**,  $\text{Ph}_3\text{SnX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) m.p.  $106^\circ$ ,  $125^\circ$ , and  $121^\circ$ , respectively, are formed by the action of the halogens on tetraphenyl-tin at  $-48^\circ$ . **Tetraphenyl-stannane hydroxide**,  $\text{Ph}_4\text{SnO}$ , is obtained by the action of  $\text{KOH}$  on the bromide. **Diphenyl-tin**,  $\text{Ph}_2\text{Sn}$ , m.p.  $130^\circ$ , is a lustrous yellow powder, obtained by the action of stannous chloride on phenyl magnesium bromide, or by the action of sodium on the dichloride (*Chambers*, Am. 48, 1054; *Krause*, Ber. 51, 912; 53, 175).

**Tetraphenyl-tin**,  $\text{Ph}_4\text{Sn}$ , m.p.  $226^\circ$ , b.p. above  $420^\circ$ , is obtained from sodium-tin and bromobenzene, or by the action of stannic chloride on phenyl magnesium bromide. It is used as a phenylating agent (*Pfeiffer*, Ber. 37, 321; *Best*, Am. 51, 1922).

*Kipping* has attempted to resolve phenyl-benzyl-tolyl-tin salts and phenyl-ethyl-butyl-tin salts into diastereomers, like their purely aliphatic analogues, with the aid of optically active acids. These efforts did not succeed owing to the fact that these compounds do not crystallise well (*J.* 1928, 2365). For alkyl-aryl-tin compounds see *Kozeshkov*, Russ. J. 5, 1158.

**Phenyl-silver**,  $\text{PhAg}$ , was obtained by *Krause*, by the action of silver chloride on phenyl-magnesium bromide. The product was not, however, quite free from silver chloride. It is a dark brown powder, unstable in the air, and even in nitrogen (Ber. 56, 2064).

**PHENYL-GOLD COMPOUNDS.** **Phenyl-gold dichloride**,  $\text{PhAuCl}_2\cdot\text{H}_2\text{O}$ , is obtained by the action of  $\text{AuCl}_3$  on benzene as yellow crystals, m.p.  $65^\circ$  (decomp.). As a secondary reaction, chlorine enters the nucleus. Homologous aryl-gold compounds are known (*Kharasch*, Am. 53, 2401, 3053).

**PHENYL-LEAD COMPOUNDS.** **Phenyl-trimethyl lead**,  $\text{PhMe}_3\text{Pb}$ , b.p. (13 mm.)  $104^\circ$ , and **phenyl-triethyl lead**,  $\text{PhEt}_3\text{Pb}$ , b.p. (12 mm.)  $135^\circ$ , is obtained

from the corresponding trialkyl lead chloride and phenyl magnesium bromide (*Grueitner*, Ber. 51, 1293). Diphenyl-lead dichloride,  $\text{Ph}_2\text{PbCl}_2$ , decomposes on heating; triphenyl-lead chloride,  $\text{Ph}_3\text{PbCl}$ , m.p. 204–206°; both are obtained from  $\text{Ph}_3\text{Pb}$  and  $\text{HCl}$ . Triphenyl-lead fluoride, m.p. 318°, is obtained by the action of  $\text{KF}$  on the bromide. Tetraphenyl-lead,  $\text{Ph}_4\text{Pb}$ , m.p. 224–225°, is obtained from bromobenzene, sodio-lead, and ethyl acetate, or by the action of  $\text{PbCl}_2$  and  $\text{PhMgBr}$ . Tetra-*o*-tolyl lead, m.p. 201–202°, is obtained from  $\text{PbCl}_2$  and *o*-tolyl-magnesium bromide (*Krause*, Ber. 55, 888; *Gilman*, Am. 49, 2315; 51, 3112; *Austin*, Am. 53, 1543, 1578, 3514).

**LEAD-TRIARYLS**,  $\text{Ar}_3\text{Pb}$  and  $\text{Ar}_2\text{Pb}_2$  are formed by the action of  $\text{PbCl}_2$  on aryl-magnesium halides if the temperature is kept low. They change into tetra-aryl compounds on heating, and are probably intermediate compounds in the formation of the tetra-aryl compounds. Triphenyl-lead,  $\text{Ph}_3\text{Pb}$ , forms pale yellow rhombohedrons. It is a stable compound which begins to decompose only at 155°. Tri-*o*-tolyl-lead, m.p. 193–240°, *p*-, m.p. 240–250°.  $\text{KMnO}_4$  in acetone oxidises these compounds to the hydroxides  $\text{Ar}_3\text{PbOH}$ . Diphenyl-lead,  $\text{Ph}_2\text{Pb}$ , is a red powder which decomposes at 100°. Phenyl-cyclohexyl-methyl-lead bromide, m.p. 93°. A number of triaryl-lead bromides have been prepared (*Krause*, Ber. 55, 888, 892; 65, 30).

## 6. THE SULPHONIC ACIDS

The aromatic hydrocarbons form sulphonic acids very readily, a fact which, like their easy nitration, distinguishes them from aliphatic compounds. The introduction of the sulphonic acid group in place of an aromatic hydrogen atom is called "sulphonation."

*Methods of formation.*—1. The sulphonic acids of the benzene hydrocarbons and those of other benzene derivatives are very readily formed merely on mixing or heating with concentrated or fuming sulphuric acid. The addition of mercury or mercuric sulphate accelerates the reaction. By this means three sulphonic acid groups can be introduced into one nucleus:



Benzene sulphonic acid is formed when benzene vapour is passed through sulphuric acid at 160–200° (Fr. Pat. 492,656, add. 22,141), or by a contact process (*Guyot*, Chim. et Ind. 2, 879). For the part played by mercury compounds and their directive influence see *Lauer*, J. pr. 138, 81.

2. The action of excess chlorosulphonic acid,  $\text{ClSO}_2\text{OH}$ , with efficient cooling, gives largely the sulphonyl chlorides (*Klaesson*, Ber. 12, 1848; *Carrara*, Ber. 22, R 739; *Ullmann*, Ber. 42, 2057). Sulphones are formed as secondary products (p. 182).

3. Sulphonic acids may be obtained from diazoamino-compounds by boiling with sulphurous acid (p. 131).

4. They may also be obtained by the oxidation of thiophenols (p. 213). This reaction proves that the sulphur of the sulphonic acid group is attached to the nucleus; cf. Vol. I, p. 170, mercaptans.

5. Sulphonic acids are formed by oxidation of sulphinic acids (p. 180).

*Properties and reactions.*—Many aromatic sulphonic acids are very soluble in water and therefore crystallise with difficulty. Such acids are better "salted out" as sodium salts by the addition of sodium chloride to their concentrated aqueous solutions (*Langmuir*, Ber. 28, 91). Some sulphonic acids can be distilled without decomposition in

a cathode-ray tube (*Krafft*, Ber. 33, 320). The fact that sulphonic acids are readily formed and dissolve readily in water is used industrially for the conversion of insoluble aromatic dyes into soluble derivatives.

1. The chlorides of the acids are obtained by the action of  $\text{POCl}_3$  or  $\text{PCl}_5$  on the alkali salts, or by the action of  $\text{PCl}_5$  on the free acids. The amides, esters, etc., are obtained from the chlorides by the same methods as in the case of the alkyl-sulphonic acids (Vol. I, p. 175). The esters can also be prepared by the Schotten-Baumann method, by shaking a mixture of the chloride and the alcohol in question with caustic soda (*Foldi*, Ber. 53, 1836). They react with alcohol at  $140\text{--}150^\circ$  forming ethers (Vol. I, p. 154). Benzene sulphonic esters are able to transfer their alkyl groups to phenols and amines on heating with them, and are thus general alkylating agents. The sulphonamides are stable and crystallise well, and are often used to characterise the sulphonic acids.

2. When dry distilled the free acids give hydrocarbons and sulphones. The same decomposition is brought about more readily by heating with conc.  $\text{HCl}$  at  $150\text{--}180^\circ$ , or by distilling the ammonium salt of the sulphonic acid, or its lead salt mixed with ammonium chloride (*Kolbe*, Ber. 16, 1468). The simplest method, however, is to pass superheated steam through the dry sulphonic acid or its solution in concentrated sulphuric acid (*Kolbe*, Ber. 19, 92).

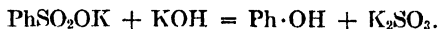
3. The  $\text{SO}_2\text{Cl}$  group of the sulphonyl chlorides can be replaced by  $\text{Cl}_2$  by means of  $\text{PCl}_5$ . In some cases the sulphonic group of the acids themselves is displaced by  $\text{Cl}_2$  or  $\text{Br}_2$  (*Kolbe*, Ber. 16, 617), but the best way to carry out this substitution is by means of  $\text{SOCl}_2$  (*Meyer*, Mo. 36, 723).

4. In some cases the sulphonic acid group can be replaced by the nitro group by treatment with nitric acid.

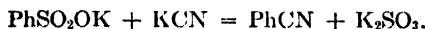
5. The sulphonic acids of alkyl-benzenes give carboxy-sulphonic acids on oxidation. Often the sulphonamides are used instead of the free acids. The oxidation of *o*-toluene sulphonamide gives *o*-sulphobenzimide, or saccharin, and is carried out commercially.

6. Reduction of aromatic sulphonyl chlorides gives thiophenols (*Fichter*, Z. Elektrochem. 13, 310):  $\text{PhSO}_2\text{Cl} + 6\text{H} = \text{PhSH} + 2\text{H}_2\text{O} + \text{HCl}$ . This reaction, like the reverse one (oxidation of thiophenol to sulphonic acid) proves that the sulphur atom is directly linked to the benzene nucleus. With alkyl-magnesium compounds the sulphonyl chlorides gives disulphoxides and thioethers (*Wedekind*, Ber. 54, 1604).

7. The sulphonic acids are unaffected by boiling aqueous alkalis. When fused with alkalis, however, they give phenols. This reaction is used in the manufacture of resorcinol (p. 222) and other phenols:



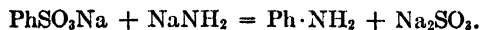
8. When distilled with dry potassium cyanide or potassium ferrocyanide, nitriles are formed:



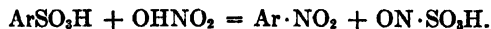
These nitriles can be hydrolysed to carboxylic acids.

9. Carboxylic acids are also obtained when the sulphonates are fused with sodium formate.

10. Primary aromatic amines (anilines) are formed when sulphonic acids are fused with sodamide (*Jackson*, Ber. 19, 903; *Sachs*, Ber. 39, 3014):



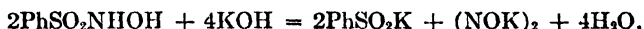
11. By the action of nitrous fumes on sulphonic acids, nitro-compounds are formed according to the equation (*Datta*, Am. 41, 2039):



**MONOSULPHONIC ACIDS.** Benzene-sulphonic acid,  $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ , m.p.  $52^\circ$ , b.p. ( $10\text{ mm.}$ )  $65^\circ$ , is exceedingly soluble in water, and crystallises from its aqueous solution with water of crystallisation. The barium salt,  $(\text{PhSO}_3)_2\text{Ba}\cdot\text{H}_2\text{O}$  forms scales with a mother of pearl lustre, and dissolves with difficulty in alcohol.

**Benzene-sulphonyl fluoride**, b.p. (14 mm.) 90–91°, is obtained from benzene and fluoro-sulphonic acid,  $F \cdot SO_3H$ , or by the action of inorganic fluorides on benzene-sulphonyl chloride (*Steinkopf*, J. pr. 117, 15). **Benzene-sulphonyl chloride**,  $PhSO_2Cl$ , m.p. 15.5–16°, b.p. (15 mm.) 119°,  $d_{25} 1.378$  (Org. Synth. I, 79) is slowly converted into the acid by boiling water. **Methyl ester**, b.p. (20 mm.) 154° (*Wegscheider*, Mo. 23, 1093). **Ethyl ester**, b.p. (15 mm.) obtained from the chloride by the action of alcohol, breaks down when heated with alcohol at 150°, into benzoic acid and ether (Vol. I, p. 155). The alkyl esters of benzene-sulphonic acids are used for replacing H atoms by alkyl groups, e.g., in acetylene (*Truchet*, Ann. Chim. [10], 16, 309). **Benzene-sulphonamide**,  $PhSO_2NH_2$ , m.p. 150°, gives an artificial resin with formaldehyde, as do also other aryl sulphonamides (Br. Pat. 342,614). **Benzene-sulphanilide**,  $PhSO_2NHPh$ , m.p. 110°. The benzene-sulphonamides of primary bases are usually soluble in alkalis, a fact which provides a method for distinguishing between primary and secondary bases (*Duden*, Ber. 33, 477; *Hinsberg*, Ber. 38, 906). The sulphonamides are decomposed into their constituents by conc. sulphuric acid (*Schroeter*, Ann. 367, 157). **Dibenzene-sulphimide**,  $(PhSO_2)_2NH$  is obtained from the action of benzene-sulphonyl chloride on sodio-benzene-sulphonamide (Ger. Pat. 125,390). **Benzene-sulpho-dichloro-amide**,  $PhSO_2NCl_2$ , m.p. 76°, is obtained by the action of  $NaOCl$  on benzene-sulphonamide,  $HCl$  and  $HI$  re-form the sulphonamide, chlorine and iodine, respectively, being evolved. Cold caustic alkalis give salts of benzenesulpho-monochloro-amide, in which the alkali metal appears to be attached to oxygen, e.g.,  $PhSO(OK):NCl$  (*Chattaway*, J. 87, 145). **Benzene-sulphonitramide**,  $PhSO_2NHNO_2$ , obtained by the action of a mixture of nitric and sulphuric acids on benzene-sulphonamide, decomposes at 100° giving benzene-sulphonic acid and nitrous oxide. Its potassium salt,  $PhSO_2NK \cdot NO_2$ , m.p. 275°, is reduced by acetic acid and zinc dust to benzene-sulphone hydrazide,  $PhSO_2NHNH_2$ , m.p. 105° (decomp.), which can also be obtained from benzene-sulphonyl chloride and hydrazine hydrate. **Benzene-sulphone phenylhydrazide**, see phenylbenzene sulphazide p. 155.

**Dibenzene-sulphone-hydrazine**,  $(PhSO_2NH)_2$ , m.p. 228°. **Benzene-sulphone azide**,  $PhSO_2N_3$ , is an oil which detonates on heating. Unlike carboxylic azides it is unattacked by hot water or alcohol. It condenses with malonic ester to 1-benzene-sulphonic-4-carboxylic-ester-5-hydroxytriazole or its keto form (*Curtius*, J. pr. 58, 160; 106, 66). **Dibenzene-sulphone-hydroxylamine**,  $(PhSO_2)_2NOH$ , is obtained from benzene-sulphonamide and nitrous acid, or from benzene-sulphinic acid (p. 180) and sodium nitrite. **Benzene-sulphono-diazobenzene-amide**,  $PhSO_2NH \cdot N:NPh$ , m.p. 101°, is obtained by the action of phenyl-diazonium chloride on benzene-sulphonamide (*Hinsberg*, Ber. 27, 598). **Benzene-sulph-hydroxamic acid**, *Piloty's acid*,  $PhSO_2 \cdot NHOH$ , m.p. 126°, obtained by the action of hydroxylamine on benzene-sulphonyl chloride, is decomposed by alkali, into benzene-sulphinic acid and hyponitrous acid (*Piloty*, Ber. 29, 1559; *Dwvrs*, Ber. 29, 2324):



Benzene sulph-hydroxamic acid reacts with aldehydes giving benzene sulphinic acid and carboxyl-hydroxamic acid (*Rimini*, Lincei [5], 10, I, 355). **Benzene-sulphone isocyanate**,  $PhSO_2NCO$ , b.p. (9 mm.) 130°, obtained by the action of silver cyanate on benzene-sulphonyl chloride, is an oil with a faint smell, and possessing all the properties and reactions of an isocyanate (*Billeter*, Ber. 37, 690).

**TOLUENE SULPHONIC ACIDS**. When toluene is sulphonated the main products are the *o*- and *p*-acids. *o*-Toluene sulphonic acid free from the *p*-isomer can be obtained by sulphonating *p*-nitrotoluene, and eliminating the nitro-group, *p*-tolyl-hydrazine-*o*-sulphonic acid being an intermediate (*Holleman*, Rec. 24, 194). The *m*-sulphonic acid is obtained from *p*-toluidine-*m*-sulphonic acid. *o*-Toluene-sulphonyl fluoride, b.p. 223–225°, *p*-toluene-sulphonyl fluoride, m.p. 41–42°. *o*-Toluene-sulphonyl chloride, b.p. (32 mm.) 151° (*Davies*, J. 119, 853, 876) may also be prepared by the action of chlorine on *o*-toluene sulphinic acid (Ger. Pat. 124,407; *Ullmann*, Ber. 38, 730). Both the *o*- and *p*-acids are obtained by the action of chlorosulphonic acid on toluene (*Harding*, J. 119, 1261). Toluene sulphonamide, m.p. 161°. *m*-Toluene sulphonic acid,  $CH_3[C_6H_4(3)]SO_3H \cdot H_2O$ , forms a liquid chloride and an amide, m.p. 108°. *p*-Toluene sul-



**phonic acid**,  $\text{CH}_3[\text{I}]\text{C}_6\text{H}_4[\text{4}]\text{SO}_3\text{H}\cdot 4\text{H}_2\text{O}$ , m.p.  $35^\circ$  (anhyd.), b.p. ( $0^\circ$  mm.)  $147^\circ$  (*Kraft*, Ber. 33, 3209), chloride, m.p.  $69^\circ$ , b.p. (15 mm.)  $145^\circ$ , bromide, m.p.  $93^\circ$ , iodide, m.p.  $84^\circ$ , amide, m.p.  $137^\circ$ , anilide, m.p.  $103^\circ$  (for kinetics of formation, see *Ebel*, Ber. 60, 2079), methyl ester, m.p.  $28^\circ$ , ethyl ester, m.p.  $33^\circ$  (*Ullmann*, Ann. 327, 121). Two substances,  $\text{Ar}\cdot\text{SO}_2\text{NCl}_2$  and  $\text{Ar}\cdot\text{SO}_2\text{N}(\text{Cl})\text{Na}$ , are obtained by chlorination of *p*-toluene sulphonamide. Both readily liberate chlorine or hypochlorous acid, and are used in surgery as substitutes for sodium hypochlorite under the names *chloramine*, *chloramine T*, *chlorazone*, or *mianine*. **Ditoluene-sulph-hydroxamic acid**,  $(\text{C}_7\text{H}_7\text{SO}_2)_2\text{NOH}$ , m.p.  $148^\circ$  (decomp.), obtained by the action of sodium nitrite on toluene sulphinic acid, gives **tritoluene-sulphone amide**,  $(\text{C}_7\text{H}_7\text{SO}_2)_3\text{N}$ , m.p.  $190^\circ$ , with another molecule of sulphinic acid (*Meyer*, J. pr. 54, 95). For further derivatives of *p*-toluene sulphonic acid see *Reverdin*, Ber. 34, 2996.

**XYLENE SULPHONIC ACIDS.** **1,2-Xylene-4-sulphonic acid**, m.p.  $54\text{--}55^\circ$  (*Anschutz*, Ber. 52, 1860); chloride, m.p.  $51^\circ$ , amide, m.p.  $144^\circ$ . **1,3-Xylene-4-sulphonic acid**, m.p.  $63^\circ$ , fluoride, b.p.  $246^\circ$  (*Davis*, J. 1931, 2104), chloride, m.p.  $34^\circ$ , amide, m.p.  $137^\circ$ . **1,3-Xylene-2-sulphonic acid**, amide, m.p.  $39^\circ$ . **1,4-Xylene-2-sulphonic acid**, m.p.  $36^\circ$ , b.p. ( $0^\circ$  mm.)  $149^\circ$ , chloride, m.p.  $25^\circ$ , amide, m.p.  $147^\circ$ . These acids are formed when xylenes are sulphonated.

**1,2,4-pseudo-Cumene-5-sulphonic acid**,  $\text{Me}_2\text{C}_6\text{H}_3\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$ , m.p.  $111^\circ$ , chloride, m.p.  $61^\circ$ , amide, m.p.  $181^\circ$ . **Mesitylene sulphonic acid**,  $\text{C}_6\text{H}_3(\text{SO}_3\text{H})\cdot 2\text{H}_2\text{O}$ , m.p.  $77^\circ$ , chloride, m.p.  $58^\circ$ , amide, m.p.  $143^\circ$ . **Cymene sulphonic acids** barium salts, *p*-cymene-2-sulphonamide, m.p.  $114\text{--}115^\circ$  (*Le Fèvre*, J. 1934, 1501).

**POLYSULPHONIC ACIDS.** **Benzene disulphonic acids**,  $\text{C}_6\text{H}_4(\text{SO}_3\text{H})_2$ . When benzene is heated with fuming sulphuric acid to  $200^\circ$ , *m*- and *p*-benzene disulphonic acids are formed, the former predominating; on continued heating, however, the meta acid is converted into para. The mutual change of the two isomers can be effected by heating with  $\text{H}_2\text{SO}_4$  and certain metals, particularly silver (*Mohrmann*, Ann. 410, 373). The *m*-disulphonic acid has been obtained from disulphanilic acid by means of the diazo-compound. *o*-Benzene disulphonic acid has been prepared by further sulphonating *m*-aminobenzene sulphonic acid, and then replacing the amino-group by H. It has also been obtained from *o*-sulphanilic acid (p. 178) by diazotising, coupling with potassium xanthogenate, heating the resulting diazonium xanthogenate, and oxidising the xanthogenic ester obtained with nitric acid (*Hollemann*, Rec. 29, 416; 40, 446). The m.p. of the chlorides and amides are given below:

|                                                               | ortho-      | meta-       | para-       |
|---------------------------------------------------------------|-------------|-------------|-------------|
| $\text{C}_6\text{H}_4(\text{SO}_2\text{Cl})_2$ , .....        | $142^\circ$ | $63^\circ$  | $141^\circ$ |
| $\text{C}_6\text{H}_4(\text{SO}_2\cdot\text{NH}_2)_2$ , ..... | $252^\circ$ | $229^\circ$ | $288^\circ$ |

When distilled with potassium cyanide or potassium ferrocyanide, the disulphonic acids form the corresponding *dicyanides*  $\text{C}_6\text{H}_4(\text{CN})_2$ , which are the nitriles of the three phthalic acids. When fused with KOH both the meta- and the para-acid give *resorcinol* or *m*-dihydroxybenzene (p. 222); at lower temperatures both give *m*-phenol sulphonic acid,  $\text{C}_6\text{H}_4(\text{OH})\text{SO}_3\text{H}$ , as the first product.

**1,3,5-Benzene trisulphonic acid**,  $\text{C}_6\text{H}_3(\text{SO}_3\text{H})_3\cdot 3\text{H}_2\text{O}$ , is easily prepared by heating potassium *m*-benzene disulphonate with sulphuric acid. Chloride, m.p.  $184^\circ$ , amide, m.p.  $310\text{--}315^\circ$ . When fused with potash the acid gives *phloroglucinol* (1,3,5-trihydroxy-benzene, p. 230), and when fused with KCN it gives a trinitrile which yields *trimesic acid*,  $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_3$ , on hydrolysis.

All six possible toluene disulphonic acids and a number of *xylene disulphonic acids* are known. **Mesitylene disulphonic acid**,  $+4\text{H}_2\text{O}$ , m.p.  $85^\circ$  (not sharp); dichloride, m.p.  $124^\circ$  (*Limpricht*, Ber. 9, 550; *Klason*, Ber. 20, 350; *Pfannenstill*, J. pr. 46, 152; *Wynne*, Proc. 1895, 152; *Backer*, Rec. 54, 544).

**Benzene selenonic acid**,  $\text{PhSeO}_3\text{H}$ , hygroscopic needles, m.p.  $142^\circ$ , is prepared by heating benzene with selenic acid at  $100\text{--}110^\circ$ , or by oxidising phenyl diselenide (p. 217) with chlorine water. When heated to  $180^\circ$  it decomposes explosively with formation of phenyl selenide and diselenide, oxygen being evolved. When reduced with hydrogen sulphide or sulphur dioxide it is converted into selenophenol. It is reduced by conc. HCl to benzene seleninic acid (p. 181) even in the cold, chlorine being set free (*Doughty*, Am. Chem. J. 41, 326).

*o*-Xylene-4-selenic acid, m.p. 108–110°; *m*-xylene-4-selenic acid, m.p. 130–130.5°; *p*-xylene-2-selenic acid, m.p. 95–96°, are obtained from the xylenes with selenic acid dissolved in acetic anhydride (*Anschütz*, Ber. 52, 1860). *m*-Nitrophenyl-selenic acid, m.p. 146° (*Pyman*, J. 115, 166).

**CHLORO-, BROMO-, IODO-, IODOSO-, NITROSO-, AND AMINO BENZENE SULPHONIC ACIDS.** The chloro-, bromo-, and iodobenzene sulphonic acids are prepared from the three aminobenzene sulphonic acids by the diazo-reaction (*Langmeier*, Ber. 28, 90). When chloro- and bromobenzenes are sulphonated, the *p*-compounds are chiefly formed. By nitrating benzene sulphonic acid or sulphonating nitrobenzene, the three isomeric nitrobenzene sulphonic acids are formed, the *m*-compound predominating (*Limpricht*, Ann. 177, 60). *o*- and *p*-Nitrobenzene sulphonic acids are better obtained by the oxidation with fuming nitric acid of the corresponding nitrobenzene disulphides (NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>, obtained from the nitrochlorobenzenes (*Ekbom*, Ber. 35, 651; *Wohlfahrt*, J. pr. 66, 551). They are separated by means of their magnesium or ferric salts (*Fierz*, Helv. 12, 663).

The following table gives the melting points of the chlorides and amides of the acids:

| Compound        | ortho-   |       | meta-    |       | para-    |       |
|-----------------|----------|-------|----------|-------|----------|-------|
|                 | Chloride | Amide | Chloride | Amide | Chloride | Amide |
| Chlorosulphonic | 28°      | 188°  | Oil      | 148°  | 53°      | 143°  |
| Bromosulphonic  | 51°      | 186°  | Oil      | 154°  | 75°      | 166°  |
| Iodosulphonic   | 51°      | 170°  | 23°      | 152°  | 87°      | 183°  |
| Nitrosulphonic  | 69°      | 191°  | 64°      | 166°  | 80°      | 178°  |

*Iodosobenzene sulphonic acid* is obtained by the action of NaOH on *o*-iodo chloride of benzene sulphonyl chloride, Cl<sub>2</sub>I[2]C<sub>6</sub>H<sub>4</sub>[1]SO<sub>2</sub>Cl, m.p. 60° (*Langmuir*, Ber. 28, 95).

*m*-Nitrosobenzene sulphonic acid (*Limpricht*, Ber. 25, 75).

*p*-Nitrotoluene-*o*-sulphonic acid H<sub>2</sub>O, m.p. 130° (anhydrous) is obtained from *p*-cymene by sulphonation and subsequent nitration (Ger. Pat. 327,051). 6-Chloro-5-nitro-*m*-toluene sulphonic acid, m.p. 47–50° (?) is used as a reagent for detecting potassium, because of the fact that its potassium salt is sparingly soluble (sensitiveness 1:2500) (*Davies*, J. 123, 2976). The nitro-group in chloro-nitrobenzene sulphonic acid can be replaced by chlorine by the action of thionyl chloride (*Meyer*, Mo. 36, 723).

**AMINO BENZENE SULPHONIC ACIDS.** (1) When aniline is sulphonated by fuming sulphuric acid (8–10% SO<sub>3</sub>) at 180°, the *p*-compound is the chief product. It is known as **sulphanilic acid**, and is very important as an intermediate in the dyestuff industry. It was discovered by *Gerhardt* in 1845. The second sulphonic acid group enters in the *o*-position, with formation of 1-aniline-2,4-di-sulphonic acid. The third sulphonic acid group enters in the *o'*-position.

Aminobenzene sulphonic acids can also be obtained (2) by reduction of the nitrobenzene sulphonic acids; (3) by heating chlorobenzene sulphonic acids with ammonia in the presence of copper salts (Ger. Pat. 205,150); (4) the sodium salts of the phenyl sulphaminic acids (p. 86) rearrange when heated to 170–180° into the salts of

aminobenzene sulphonic acids (*Seyewitz*, Bull. 1, 320). Like glycocholic and taurine (Vol. I, pp. 376, 440) the aminobenzene sulphonic acids

are to be regarded as inner ammonium salts:  $\text{C}_6\text{H}_4 \begin{matrix} \text{SO}_3^- \\ \text{NH}_3^+ \end{matrix}$

For the so-called "baking" process (heating the acid sulphate of the amine to a high temperature), which takes a somewhat different course from the first reaction mentioned above, see *Huber*, Helv. 15, 1372.

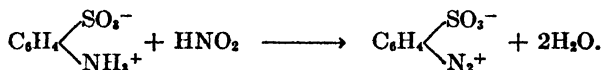
All three aminobenzene sulphonic acids are very difficultly soluble in cold water, and are insoluble in alcohol and ether. The *ortho*-acid, known as "*orthanilic acid*," crystallises either anhydrous in rhombohedra, or with  $\frac{1}{2}\text{H}_2\text{O}$  in four-sided prisms, which do not effloresce. It is best obtained from *o*-nitrobenzene sulphonic acid or from *p*-bromoaniline-*o*-sulphonic acid by reduction (*Scott, Cohen*, J. 121, 2034). The *meta*-acid, also known as "*metanilic acid*," which is important in the manufacture of dyes, crystallises in slender needles, or with  $\frac{1}{2}\text{H}_2\text{O}$ , in efflorescing prisms. *o*-**Sulphanilic acid** crystallises with  $2\text{H}_2\text{O}$  in rhombic tablets, which effloresce in air, and dissolve in 112 parts of water at  $15^\circ$  (*Laar*, Ber. 14, 1933). When oxidised with manganese dioxide and sulphonic acid or with chromic acid, quinone is formed. When fused with KOH it gives aniline and not aminophenol. In contrast to its isomers, it is readily converted into tribromoaniline by bromine water (*Breuzinger*, Ber. 29, R. 309).

**Sulphanilamide**, *prontosil album*, has recently been introduced into medicine as a specific for puerperal fever, and other streptococcal infections.

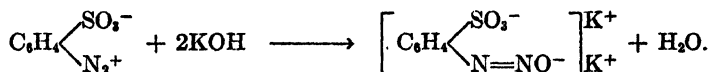
The sodium salts of the aminobenzene sulphonic acids, but not the free acids themselves, are converted into *acetyl derivatives* by the action of acetic anhydride (*Nietzki*, Ber. 17, 708; *Schroeter*, Ber. 39, 1561). This fact agrees with the ammonium salt formula for the free acids (see above).

By the action of nitric acid, the sulphonic acid group of the *o*- and *p*-acids is replaced by the nitro-group, and nitranilines are formed (*Zincke*, Ann. 339, 202). The halogen group can be introduced in a similar way (*Sudborough*, J. 111, 41). For the introduction of nitroso-groups into the nucleus of *N*-alkylamino-benzene sulphonic acids, see *Houben*, Ber. 53, 2346. *p*-**Phenylene-diamino-monosulphonic acid**,  $\text{C}_6\text{H}_4(\text{SO}_3\text{H})(\text{NH}_2)_2$ , is obtained by heating *p*-dichlorobenzene sulphonic acid with ammonia in the presence of copper bronze (Ger. Pat. 202,564/5). **Toluylene-diamino-sulphonic acids**, see *Bueckel*, C. 1904, I, 1410. **Trisulphanilic acid**, 1-amino-2,4,6-trisulphonic acid +  $4\text{H}_2\text{O}$ , is obtained by the action of  $\text{H}_2\text{SO}_4$  +  $\text{P}_2\text{O}_5$  on sulphanilic acid at  $180^\circ$  (*Oliver*, Rec. 39, 194).

**PHENYL-DIAZONIUM SULPHONIC ACID BETAINES.** By the action of nitrous acid on the three aminobenzene sulphonic acids their ammonium cation is converted into the diazonium cation:



Like all diazonium salts these diazonium betaines form the corresponding diazotates and the alkali salt of the anion when treated with two equivalents of alkali. Since the anion of the diazonium salt is linked to the benzene nucleus by an atomic linkage, these diazotates contain two alkali metal ions to each benzene nucleus:



These di-potassium and di-sodium salts of the *o*- and *p*-diazobenzene sulphonic acids each exists in two forms, one of which belongs to the *n*- and the other to the *iso*-series (p. 118). The *iso*-salts may be obtained from the normal salts by heating. They less readily give off nitrogen and couple only with difficulty or not at all (*Hantzsch*, Ber. 29, 1059; *Bamberger*, Ber. 29, 1388). **Primary potassium hydrogen *iso*-diazosulphonate**,  $\text{C}_6\text{H}_4(\text{SO}_2\text{K})\text{N}_2\text{OH} + \text{H}_2\text{O}$  is obtained by the

action of acetic acid on the di-potassium salt. While the formation of internal anhydrides with ring closure is practically confined to ortho di-derivatives of benzene, the formation of internal ammonium salts, such as the diazonium-sulphobetaines, N-trialkyl benzene betaines (p. 329) and -cinnamic betaines, are formed with equal readiness from meta- and para-compounds. This shows that there is no ring-closure in the formation of betaines. According to modern theory the line between the "onium" cation and the anion is not covalent, but electrovalent, the attraction being electrostatic. The betaines are thus "zwitter" ions (Pfeiffer, Ber. 55, 1762). The diazonium betaines of the aniline sulphonic acids show the reactions of diazonium salts. *p*-Diazobenzene sulphonic acid forms white needles, difficultly soluble in water. Although fairly stable as diazonium compounds go, it is likely to explode spontaneously (Wichelhaus, Ber. 34, 11). When heated with alcohol it gives benzene sulphonic acid; with water it gives *p*-phenol sulphonic acid; and with potassium sulphide, the di-potassium salt of *p*-thiophenol sulphonic acid. For the action of bleaching powder on diazobenzene sulphonic acid, see Zincke, Ann. 330, 1. The diazonium compound,  $\text{C}_6\text{H}_5\begin{matrix} \text{N}_2^+ \\ \text{SO}_2\text{NH}^- \end{matrix}$ ,

which explodes mildly on heating, has an intensely sweet taste (cf. saccharin, p. 333). The replacement of the CO group of saccharin by  $\text{N}_2$  does not affect the taste (Fierz, Helv. 12, 663).

**AMINOAZOBENZENE SULPHONIC ACIDS.** The diazonium betaines of sulphanilic acid and metanilic acid may be used for the preparation of **sulphonated azo-dyes**. The first group of this large class of dyes has already been dealt with (p. 138). It comprises the aminoazo-compounds which are difficultly soluble or insoluble in water. If sulphonic acid groups are introduced into aminoazo-compounds, the solubility increases with the number of such groups. The alkali salts of the aminoazobenzene sulphonic acids are dyes soluble in water. Other groups of azo-dyes will be met with under phenols (*hydroxyazo-compounds*). The naphthalene azo-compounds and the *benzidine dyes* which contain a diphenyl radical, are particularly important.

The azo-dyes are usually given arbitrary names with the letters Y (yellow), O (orange), and R (red) attached. The number of letters attached indicates roughly the intensity of the colour. Wool and silk are dyed directly, but cotton must, as a rule, be mordanted (p. 138).

**Preparation.**—1. By sulphonation of aminoazo-compounds. 2. By combining the diazonium betaines of sulphonic acids with bases.

When aminoazobenzene is sulphonated, a mixture of aminoazobenzene mono- and di-sulphonic acids is formed, which is known commercially as "acid yellow" or "fast yellow." Their formulae are  $\text{SO}_3\text{H}[4]\text{C}_6\text{H}_4[1]\text{N}:\text{N}[1']\text{C}_6\text{H}_4[4']\text{NH}_2$  and  $\text{SO}_3\text{H}[4]\text{C}_6\text{H}_4[1]\text{N}:\text{N}[1']\text{C}_6\text{H}_4[4']\text{NH}_2[3']\text{SO}_3\text{H}$  (Eyer, Ber. 22, 847). Since they are amino-compounds the sulphonic acids themselves are again capable of diazotisation and coupling. By this method some valuable *bis*-azo-dyes, such as *Biebrich scarlet*, are obtained. For aminoazobenzene trisulphonic acid, see Junghahn, Ber. 33, 1366.

The following azo-dyes are obtained by coupling diazotised sulphanilic acid with dimethylaniline, or diphenylamine, and diazotised metanilic acid with diphenylamine:

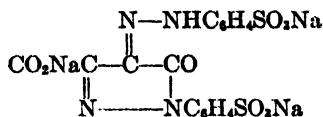
**4'-Dimethylaminoazobenzene-4-sulphonic acid**,  $\text{SO}_3\text{H}[4]\text{C}_6\text{H}_4[1]\text{N}:\text{N}[1]\text{Cl}$ ,  $\text{H}_4[4']\text{NMe}_2$  or  $-\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{C}_6\text{H}_4\cdot\text{N}^+\text{Me}_2$  (see p. 178), m.p. 115°, golden-yellow leaflets (Griess, Ber. 10, 528; Hantzsch, Ber. 41, 1187). Its sodium salt is the dye *tropaeolin O*, *orange III*, or *helianthin*. This dye is used as an indicator in alkalimetry; mineral acids change the yellow alkaline solution into the pink acid colour, but carbon dioxide, hydrogen sulphide, and acetic acid do not affect it in the cold (Lunge, Ber. 18, 3290). Helianthin is decomposed by reduction into sulphanilic acid and *p*-aminodimethylaniline (p. 107). With fuming nitric acid it is broken down into phenyldiazonium sulphonic acid betaine and 2,4-dinitrodiphenylamine (Schmidt, Ber. 38, 3206; Fox, Ber. 41, 1989). For its decomposition by chlorine, bromine, and hypochlorous acid, see Schmidt, J. pr. 85, 235).

**4'-Phenylaminoazobenzene-4-sulphonic acid**,  $\text{SO}_3\text{H}[4]\text{C}_6\text{H}_4[1]\text{N}:\text{N}[1]\text{C}_6\text{H}_4[4']\text{NHPh}$ . The sodium salt of this compound dyes wool and silk a beautiful orange colour, and is used under the name of *tropaeolin O*, *orange IV*, or *diphenyl-*

*amine orange*. For its use as an indicator, see *Wieland*, Ber. 16, 1989. When reduced it breaks down into sulphanilic acid and *p*-aminodiphenylamine.

4'-Phenylaminoazobenzene-3-sulphonic acid is obtained from metanilic acid and is used under the name of *metaniline yellow*.

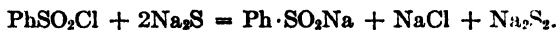
**PHENYLHYDRAZINO-SULPHONIC ACIDS** are formed by the reduction of the diazides of aniline-sulphonic acids with sodium sulphite or stannous chloride (Ber. 22, R 216) and by the direct action of concentrated sulphuric acid on phenyl hydrazines (*Gallinek*, Ber. 18, 3172). Phenylhydrazino-*p*-sulphonic acid,  $C_6H_4(N_2H_2)SO_3H$ , forms crystals which are sparingly soluble in water, and is used in the preparation of *tartrazine* (Vol. I, p. 663). It has the structure:



(see Vol. I, p. 663; Vol. IV).

**Hydrazobenzene-*m*-disulphonic acid**,  $SO_3H[3]C_6H_4[1]NH-NH[1]C_6H_4[3']SO_3H$ , has been obtained by the reduction of *m*-nitrobenzene sulphonic acid. Hydrochloric acid converts it into benzidine disulphonic acid (Ber. 21, R 323; 23, 1053).

**SULPHINIC ACIDS. Methods of formation.**—1. By the action of zinc dust on the ether solutions of the sulphonyl chlorides. 2. By the action of hot aqueous solutions of alkaline sulphides on sulphonyl chlorides:



3. By the action of copper powder on a solution of a diazonium salt saturated with sulphur dioxide (p. 124 and *Gattermann*, Ber. 32, 1136; Ger. Pat. 130,119):



4. By the action of sulphur dioxide on benzene in the presence of aluminium chloride. The compound  $\text{C}_6\text{H}_5\text{SO}_2\text{AlCl}_3$  is apparently produced as an intermediate product. The reaction proceeds very smoothly (*Gutmann*, Ber. 41, 3315). If phenol ethers are used in this reaction sulfoxides (p. 182) and sulphonium bases are chiefly formed, together with sulphinic acids (*Smiles*, J. 93, 745).

5. By the action of sulphur dioxide or thionyl chloride on phenyl-magnesium bromide (*Rosenheim*, Ber. 37, 2153; *Oddo*, Lincei 14, I, 169). 6. By the action of sodium on sulphones (*Krafft*, Ber. 26, 2813). 7. By the action of potassium cyanide or sodium arsenite on the benzene thiosulphonates (*Hinsberg*, Ber. 41, 3351). 8. By the decomposition of benzene sulph-hydroxamic acids (p. 175).

**Reactions.**—The sulphinic acids are not very stable, and decompose when warmed with water into sulphonic acids and disulphoxides (p. 182). They are oxidised in the air, and by oxidising agents, particularly barium peroxide or potassium permanganate, to sulphonic acids. By reduction with zinc dust and sulphuric acid they are converted into thiophenols (p. 213). Their salts combine with sulphur to give thiosulphonates. When fused with alkali they decompose into benzene hydrocarbons and alkali sulphites. With hydrogen bromide they give aryl sulphobromides, or if these are unstable under the conditions of formation, aryl disulphides (p. 215) (*Fries*, Ber. 47, 1195). With thionyl chloride they give *sulphinic chlorides* (*Hilditch*, Ber. 41, 4114), and with acetic anhydride *sulphinic anhydrides* (*Knoevenagel*, Ber. 41, 3323). They combine with aldehydes to give unstable *hydroxysulphones*,  $\text{CH}_3\text{CH}(\text{OH})\text{SO}_2\text{Ph}$ . Like  $\text{SO}_2$  they add on to  $\alpha,\beta$ -unsaturated aldehydes, ketones, and carboxylic acids, forming sulphones, such as  $\text{PhCH}(\text{SO}_2\text{Ph})\text{CH}_2\text{COOH}$  (*Köhler*, Am. Chem. J. 31, 163). Benzene sulphinic acid combines with quinone to give *as-p*-dihydroxydiphenyl-sulphone,  $(\text{HO})_2[2,5]C_6H_3[1]SO_2\text{Ph}$  (*Hinsberg*, Ber. 27, 3259), and with a number of other

substances containing quinoid linkages (*cf. Hinsberg, Ber. 29, 2019*). It also reacts with *o*- and *p*-dihydroxybenzenes (p. 218) with the formation of dihydroxydiphenyl-sulphones. Phenol gives hydroxydiphenyl sulphide,  $\text{HOC}_6\text{H}_4\text{SPh}$ , among other products, and similarly aniline hydrochloride gives aminodiphenyl sulphide,  $\text{H}_2\text{NC}_6\text{H}_4\text{SPh}$  (*Hinsberg, Ber. 36, 107*).

The alkali sulphinates form mixed sulphones with alkyl iodides (p. 183), and true sulphinic esters with chlorocarbonic esters (*Otto, Ber. 26, 308, 430*):



In acid solution the sulphinic acids give difficultly soluble ferric salts with ferric chloride; these can be used for isolating the sulphinic acids from a reaction mixture (*Thomas, J. 95, 342*).

**Benzene sulphinic acid**,  $\text{PhSOOH}$ , m.p.  $83^\circ$ ; zinc salt,  $(\text{PhSO}_2)_2\text{Zn} \cdot 2\text{H}_2\text{O}$ ; ethyl ester  $d_{20} 1.141$ , decomp. on heating. **Benzene sulphinic anhydride**,  $(\text{PhSO})_2\text{O}$ , m.p.  $67^\circ$ , breaks down after a short time with formation of benzene sulphonic acid and phenyl-benzenethiosulphonate,  $\text{PhSO}_2\text{SPh}$ . **Benzene sulphinyl chloride**,  $\text{PhSOCl}$ , colourless tablets, m.p.  $38^\circ$ , fumes in air and is rapidly decomposed by water, benzene sulphinic acid being formed. On warming, or treatment with concentrated sulphuric acid, the chloride, and also the free acid, undergo an intramolecular condensation to diphenylene-disulphoxide,

$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{SO} \diagdown \\ \diagdown \text{SO} \diagup \end{array} \text{C}_6\text{H}_4$ , and other polymerisation products (*Hilditch, J. 97, 2579*).

**Benzene sulphinic anilide**, m.p.  $115^\circ$ , is obtained from thioaniline (p. 86) and phenyl magnesium bromide (*Gilman, Am. 48, 2399*).

***o*-Nitrobenzene sulphinic acid**, m.p.  $134^\circ$ , is obtained from *o*-nitrobenzene sulphonyl chloride by reduction with stannous chloride and  $\text{HCl}$  (*Claasz, Ann. 380, 303*).

***o*- and *p*-TOLUENE SULPHINIC ACIDS**,  $\text{C}_6\text{H}_4(\text{CH}_3)\text{SOOH}$ , m.p.  $80^\circ$  and  $85^\circ$  (*cf. Troeger, J. pr. 54, 517; Haellsig, J. pr. 56, 213*). Further homologues, *Gattermann, Ber. 32, 1140*. Optically active ethyl esters of these acids have been prepared by *Phillips, J. 127, 2552; Clarke, J. 1927, 180*. In these compounds the sulphur atom is the centre of asymmetry. The stereoisomerism of these esters and the sulfoxides indicates a non-polar arrangement of the groups attached to

sulphur. According to the classical formulation  $\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{OH}$ ,  $\text{R}-\overset{\text{O}}{\text{C}}-\text{OH}$ ,  $\text{R}-\overset{\text{O}}{\text{S}}-\text{R}$ ,  $\text{R}-\overset{\text{O}}{\text{C}}-\text{R}$  sulphinic and carboxylic acids are analogous to sulfoxides

and ketones. The octet formulation  $\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O}-\text{H}$ ,  $\text{R}-\overset{\text{O}}{\text{C}}-\text{O}-\text{H}$ ,  $\text{R}-\overset{\text{O}}{\text{S}}-\text{R}$ ,

$\text{R}-\overset{\text{O}}{\text{C}}-\text{R}$  makes clear the difference between the C- and S-compounds. Dimethyl and diethylaniline sulphinic acids,  $\text{R}_2\text{NC}_6\text{H}_4\text{SO} \cdot \text{OH}$ , are produced by the action of thionyl chloride on dimethyl- and diethyl-aniline (*Michaelis, Ann. 310, 137*). **Benzene disulphinic acid**,  $\text{C}_6\text{H}_4(\text{SO}_2\text{H})_2$  (*Troeger, Ber. 35, 2168; Authenrieth, Ber. 36, 189*).

**Benzene seleninic acid**,  $\text{PhSeOOH}$ , m.p.  $124-125^\circ$ , is prepared by oxidising diphenyl diselenide (p. 217) with nitric acid, or by treating benzene selenonic acid with  $\text{HCl}$  (p. 176). When heated to  $130^\circ$  it gives the anhydride,  $(\text{PhSeO})_2\text{O}$ , m.p.  $164^\circ$  (*Doughty, Am. Ch. J. 41, 326; Pyman, J. 115, 166*). ***m*-Nitrobenzene seleninic acid**, m.p.  $156-157^\circ$ .

**BENZENE SULPHENIC ACIDS**. These are compounds of the type  $\text{Ar} \cdot \text{S} \cdot \text{OH}$ . They are prepared from the sulpho-chlorides,  $\text{Ar} \cdot \text{SCl}$ , the sulphenic chlorides (obtained by chlorinating mercaptans, p. 213), or phenyl disulphides (p. 215). The free acids do not exist; only derivatives such as chlorides,  $\text{ArSCl}$ , anhydrides,  $(\text{ArS})_2\text{O}$ , alkyl esters,  $\text{ArS} \cdot \text{OAlk}$ , and amides,  $\text{ArS} \cdot \text{NH}_2$ , being known (*Zincke, Ann. 391, 55*).

**Phenyl sulphochloride**,  $\text{PhSCl}$ , b.p. (3 mm.)  $58-60^\circ$ , is a red liquid with the appearance of sulphur chloride. It is obtained by the action of chlorine on thiophenol (*Lecher*, Ber. 57, 755). **Methyl benzene sulphenate**,  $\text{PhSOCH}_3$ , b.p. (4 mm.)  $88-89^\circ$ , is obtained from phenyl sulphochloride and sodium methylate. **Benzene sulphenic dimethyl amide**,  $\text{PhSN}(\text{CH}_3)_2$ , b.p. (3 mm.),  $64^\circ$ , is obtained from the chloride by the action of dimethylamine. **Benzene sulphenic anilide**,  $\text{PhSNHPh}$ , m.p.  $53-55^\circ$ ; **-imide**,  $(\text{Ph}\cdot\text{S})_2\text{NH}$ , m.p.  $127-128^\circ$  (decomp.). The hydrazine,  $(\text{PhS})_2\text{N}\cdot\text{N}(\text{SPh})_2$ , can be obtained from the imide, and this, on oxidation, gives the free radical  $(\text{PhS})_2\text{N}\cdot$  (*Lecher*, Ber. 57, 755; 58, 423).

***o*-Nitrophenyl sulphochloride**, golden yellow needles, m.p.  $75^\circ$ ; **bromide**, m.p.  $85^\circ$  (*Zincke*, Ann. 391, 55). ***p*-Nitrophenyl sulphochloride**, yellow flakes, m.p.  $52^\circ$ . **Methyl *p*-nitrophenyl-sulphenate**, m.p.  $49^\circ$  (*Zincke*, Ann. 400, 1). ***p*-Tolyl sulphochloride**, b.p. (25 mm.)  $78^\circ$  (*Zincke*, Ann. 400, 1; *Lecher*, Ber. 58, 412).

**Phenyl selenobromide**,  $\text{PhSeBr}$ , m.p.  $62^\circ$ , is obtained by brominating phenyl selenocyanide, b.p. (17 mm.)  $127^\circ$ , itself prepared by the action of potassium selenocyanate on diazotised aniline (*Behagel*, Ber. 65, 815).

**Benzene thiosulphonic acid**. The salts of this acid are obtained by the action of alkali sulphides on benzene sulphonyl chloride, or by the action of sulphur on the benzene sulphinates (*Otto*, Ber. 25, 1477). The thiosulphonic acids combine with organic bases to give salts which usually crystallise well (*Troeger*, J. pr. 60, 113).

**DISULPHOXIDES OR THIOSULPHONIC ESTERS**. Alkyl and alkylene esters of benzene thiosulphonic acid are obtained from its potassium salt by the action of the corresponding bromides. **Phenyl thiosulphone acetoacetic ester**,  $\text{PhSO}_2\text{S}\cdot\text{CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5$ , m.p.  $56^\circ$ , is obtained from chloroacetic ester and potassium benzene thiosulphonate (*Raalle*, Rec. 18, 378).

The phenyl esters of thiosulphonic acids are obtained (1) by the oxidation of thiophenols with nitric acid; (2) by the oxidation of disulphides (p. 215) with hydrogen peroxide (*Hinsberg*, Ber. 41, 2838); (3) by heating sulphinic acids with water at  $130^\circ$ . **Benzene disulphoxide**,  $\text{PhSO}\cdot\text{SOPh}$ , or  $\text{Ph}\cdot\text{SO}_2\text{SPh}$ , m.p.  $45^\circ$ , is insoluble in water, but dissolves readily in alcohol and ether (*Otto*, Ber. 20, 2090).

**Sulphobenzene sulphide**,  $(\text{PhSO}_2)_2\text{S}$ , m.p.  $133^\circ$ . **Sulphobenzene disulphide**,  $(\text{PhSO}_2)_2\text{S}_2$ , m.p.  $76^\circ$ . **Sulphobenzene trisulphide**,  $(\text{PhSO}_2)_3\text{S}_3$ , m.p.  $103^\circ$ . Polythio-compounds of this kind are obtained by the action of iodine or chlorine on benzene thiosulphonates and by the action of sulphur chlorides on the benzene sulphinates and benzene thiosulphonates (*Otto*, Ber. 24, 1141; 25, 1477; *Troeger*, J. pr. 60, 113).

**DISULPHONES**, such as **diphenyl disulphone**,  $\text{PhSO}_2\cdot\text{SO}_2\text{Ph}$ , m.p.  $194^\circ$ , **phenyl-*p*-tolyl disulphone**,  $\text{PhSO}_2\cdot\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$ , m.p.  $166^\circ$ , and **di-*p*-tolyl disulphone**,  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\cdot\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$ , m.p.  $221^\circ$  (decomp.), are formed by the action of sulphinates on sulphochlorides, and in small yield and together with sulphonic acids by the oxidation of benzene sulphinic acids with potassium permanganate (*Hilchich*, J. 93, 1524). On heating with alkalis they decompose into a mixture of sulphinates and sulphonates.

**SULPHOXIDES**. Mixed aromatic-aliphatic sulphoxides are formed when aryl-alkyl sulphides are oxidised with hydrogen peroxide (p. 216) (*Hinsberg*, Ber. 41, 2836; *Gazdar*, J. 93, 1833) or when their dibromo-addition products are acted upon by water.

**Phenyl-sulphoxy-acetic acid**,  $\text{PhSOCH}_2\text{COOH}$ , m.p.  $116^\circ$ , is decomposed by heating with mineral acids to thiophenol (p. 213) and glycolic acid.

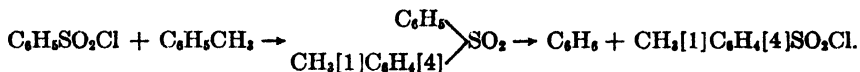
**Diphenyl-sulphoxide**,  $\text{Ph}_2\text{SO}$ , m.p.  $70^\circ$ , is obtained (1) from benzene by the action of sulphur dioxide or thionyl chloride and aluminium chloride (*Colby*, Ber. 20, 195; *Loth*, Ber. 27, 2547); (2) from diphenyl sulphide by oxidation with hydrogen peroxide (*Hinsberg*, Ber. 43, 289); (3) by the action of thionyl chloride or diethyl sulphite on phenyl magnesium bromide (*Strecker*, Ber. 43, 1135); (4) by the action of water on diphenyl-sulphide halides,  $\text{Ph}_2\text{SX}_2$  (*Fries*, Ann. 381, 337). It is oxidised to diphenyl sulphone by permanganate. **Diphenyl-selenoxide**,  $\text{Ph}_2\text{SeO}$ , is prepared by oxidising diphenyl selenide (p. 217) or from the dibromide of the latter (*Krafft*, Ber. 29, 424).

**SULPHONES**. The alkyl-aryl sulphones are isomeric with the alkyl-sulphinic esters, and can be obtained by the action of alkyl halides on the sodium sulphinates. The true aromatic sulphones are formed (1) together with sulphonic acids,

by the action of sulphur trioxide or chlorosulphonic acid on benzene hydrocarbons:



(2) together with hydrocarbons, in the distillation of sulphonic acids; (3) by the oxidation of sulphides; (4) by heating benzenes or benzene sulphonic acids with  $\text{P}_2\text{O}_5$ ; (5) by the action of zinc dust or aluminium chloride on a sulphonyl chloride mixed with a benzene hydrocarbon:



The same phenyl-*p*-tolyl-sulphone is obtained from benzene sulphonyl chloride and toluene as from *p*-toluenesulphonyl chloride and benzene, which proves that both groups are linked to sulphur (Ber. 11, 2181).

(6) Nitro-derivatives of sulphones are readily formed from *o*- and *p*-chloronitrobenzenes by the action of sulphinates (Ullmann, Ber. 34, 1150).

(7) Hydroxy- and amino-derivatives of sulphones are formed by the combination of sulphinic acids with quinone and quinone-imine derivatives, etc. (p. 180).

**Phenyl-ethyl-sulphone**,  $\text{PhSO}_2\text{Et}$ , m.p.  $42^\circ$ , b.p. above  $300^\circ$ ; **phenyl-sulphone-ethyl alcohol**,  $\text{PhSO}_2\text{CH}_2\text{CH}_2\text{OH}$ , is a syrup, obtained from ethylene chlorhydrin and sodium benzene sulphinate, or from ethylene-diphenyl-disulphide,  $\text{PhSO}_2\text{---CH}_2\text{---CH}_2\text{---SO}_2\text{Ph}$ , m.p.  $180^\circ$ , by the action of conc.  $\text{NaOH}$ . On oxidation, phenylsulphone-ethyl-alcohol gives phenylsulphone-acetic acid,  $\text{PhSO}_2\text{CH}_2\text{COOH}$ , m.p.  $112^\circ$ , which is decomposed by  $\text{KOH}$  into  $\text{CO}_2$  and phenyl-methyl-sulphone,  $\text{PhSO}_2\text{Me}$ , m.p.  $88^\circ$ . **Phenylsulphone-acetamide**,  $\text{PhSO}_2\text{CH}_2\text{CONH}_2$ , m.p.  $156^\circ$ , is obtained from sodium benzene sulphinate and chloro-acetamide (Troeger, J. pr. 71, 201). **Phenylsulphone-acetonitrile**,  $\text{PhSO}_2\text{CH}_2\text{CN}$ , m.p.  $114^\circ$ . The hydrogen atoms of the  $\text{CH}_2$  group in the esters and nitrile of phenylsulphone-acetic acid can be replaced by sodium, and this by alkyl groups (Otto, Ber. 22, 1447; Michael, J. pr. 60, 96; Troeger, J. pr. 72, 323). **Phenyl-allyl-sulphone**,  $\text{PhSO}_2\text{---C}_3\text{H}_5$ , is an oil (Otto, Ann. 283, 185).  $\alpha$ - and  $\beta$ -Phenylsulphone-propionic acids, m.p.  $115^\circ$  and  $123^\circ$  (Otto, Ber. 21, 89), and numerous other mixed fatty-aromatic sulphones have been prepared (Troeger, J. pr. 66, 130).

**Diphenyl-sulphone**,  $\text{Ph}_2\text{SO}_2$ , m.p.  $128^\circ$ , b.p.  $276^\circ$ , is formed in the distillation of benzene sulphonic acid, and on oxidation of diphenyl sulphide,  $\text{Ph}_2\text{S}$  (p. 215) and diphenyl sulphoxide (see above); from benzene sulphochloride,  $\text{PhSO}_2\text{Cl}$  and mercury diphenyl; and from benzene by the action of aluminium chloride and benzene-sulphochloride or sulphuryl chloride (Töhl, Ber. 26, 2940). It is prepared by treating benzene with fuming sulphuric acid or sulphur trioxide. When heated with conc. sulphuric acid it is converted into benzene sulphonic acid, and when heated with phosphorus pentachloride or in a current of chlorine it is converted into chlorobenzene and benzene sulphochloride. With sulphur it gives diphenyl sulphide, and with selenium, diphenyl selenide (Krafft, Ber. 26, 2813). With sodium it gives benzene sulphinate and diphenyl (Krafft, Ber. 26, 2813). *o*- and *p*-Nitro-diphenyl-sulphones,  $\text{NO}_2\text{---C}_6\text{H}_4\text{---SO}_2\text{Ph}$ , m.p.  $147^\circ$  and  $143^\circ$ , and 2,4,6-trinitrodiphenyl-sulphone,  $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{SO}_2\text{Ph}$ , m.p.  $233^\circ$ , are obtained from *o*- and *p*-nitrochlorobenzene and picryl chloride, respectively, and sodium benzene sulphinate.

**Diphenyl-selenone**,  $\text{Ph}_2\text{SeO}_2$ , m.p.  $155^\circ$ , b.p.  $271^\circ$ , is obtained by the oxidation of diphenyl-selenoxide with permanganate (Krafft, Ber. 29, 424). When heated it deflagrates, oxygen is evolved, and diphenyl selenide, a very stable substance, is formed (p. 217).

For **sulphonium**, **selenonium**, and **telluronium** bases, see p. 216.

## 7. PHENOLS

The phenols are derived from the aromatic hydrocarbons by the replacement of hydrogen atoms of the benzene nucleus by hydroxyl groups. Just as in the case of alcohols, mono-, di-, and poly-hydric



phenols are distinguished according to the number of hydroxyl groups introduced. All the six hydrogen atoms of benzene can be replaced by hydroxyl groups.

The phenols correspond to the tertiary alcohols and to the enol forms of carbonyl compounds since they cannot be oxidised to ketones or acids with the same number of carbon atoms. They differ from the alcohols owing to the negative nature of the phenyl group, and this difference becomes more marked when negative groups are introduced into the benzene ring (see picric acid, p. 200; *Raikov*, C. 1903, I, 326; II, 717). On the other hand, the aromatic alcohols in which hydroxyl replaces the hydrogen of the aliphatic side-chain resemble the aliphatic alcohols much more closely.

A number of phenols have been detected in plants, and some phenol sulphonic acids are found in the urine of mammals. In the animal organism some aromatic compounds are oxidised to phenols. Thus, benzene is oxidised to phenol, bromobenzene to bromophenol, aniline to aminophenol, and phenol itself to hydroquinone. Phenols have also been found among the products of putrefaction of proteins.

Phenols are produced in the dry distillation of wood, especially beech-wood, and also in the distillation products of peat, lignite, and coal. For the phenols occurring in coal-tar, see the table on p. 36 and *Kruber*, Ber. 64, 2270.

They are isolated from tar by shaking with caustic soda in which they dissolve, and precipitating again by acids, followed by distillation.

Many phenols, including the monoalkyl ethers of dihydric phenols, combine with anhydrous neutral salts (such as calcium halides, potassium salts of the lower fatty acids) to give compounds which crystallise well, and which are decomposed into their components by the addition of water (*Weinland*, Ber. 52, 147). Another method of isolating phenols from mixtures consists in combining them with acids, such as boric, phosphorous, or arsenious acids, with which they give non-volatile esters. The volatile constituents of the mixture are removed by distillation, and the phenols recovered by alkaline hydrolysis of the residue (Br. Pat. 252,570).

### Monohydric Phenols

In addition to the methods of formation mentioned above, the following may be used: (1) decomposition of diazonium compounds, particularly sulphates, by boiling with water or copper sulphate solution (p. 124). (2) Fusion of sulphonic acids with NaOH, KOH, or alkaline earth hydroxides.



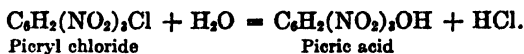
This reaction was discovered in 1867 by *Kekulé*, *Würtz*, and *Dusart*, independently of each other.

This method is used commercially for the manufacture of phenols, and is carried out in iron vessels. In the laboratory the fusion is carried out in silver or nickel dishes, the melt being dissolved in water, and an excess of acid added. The phenol is then extracted with ether (*Willson*, Ber. 47, 3160; Br. Pat. 218,034).

When sulphonic acids or phenols containing halogen atoms in the nucleus are fused with alkali, the halogen is also replaced, with formation of polyhydric phenols. Occasionally the sulphonic acid group splits off as sulphate, and is replaced by hydrogen. In this way cresol sulphonic acid yields cresol.

(3) Halogen substituted hydrocarbons react with dilute solutions of alkalis to form phenols, but the reaction requires a high temperature (300–350°) and a pressure of 280 atmos. (*Meyer*, Ber. 47, 3155; U. S. Pat. 1,833,485). Certain catalysts, especially base metals, greatly accelerate the reaction (Br. Pat. 218,034). In some cases, and with special catalysts, such as iron free  $\text{Al}_2\text{O}_3$  + Cu or Co, or porous material like pumice or chalk impregnated with  $\text{CuCl}_2$ , water alone, without the addition of alkali, will bring about the substitution (*Woroshzov*, C. 1934, II, 2523; Fr. Pats. 709,184 and 720,720). The magnesium compounds of halogenated benzene hydrocarbons are oxidised to phenols on exposure to air (*Ivanov*, Bull. 39, 47).

The reactivity of the halogen atom is greatly enhanced by the presence of one, and still more of several nitro-groups (p. 62), recalling the behaviour of acid chlorides:



(4) The amino-group in nitro-amino-compounds is similarly replaced by hydroxyl on boiling with aqueous solutions of alkalis. *o*- and *p*-Nitrilanilines,  $\text{C}_6\text{H}_4(\text{NO}_2)\text{NH}_2$  give the corresponding nitrophenols, but the *m*-compound does not. *o*-Dinitro-compounds react similarly.

(5) Small quantities of phenol are formed from benzene by the action of ozone, hydrogen peroxide, shaking with sodium hydroxide and air (*Nencki*, Ber. 14, 1144), and by oxygen in the presence of aluminium chloride. Under high pressure, toluene is oxidised to benzyl alcohol, benzaldehyde, and 2,4-dihydroxy-toluene. Ethyl benzene is first attacked at the  $\alpha$ -C-atom of the side chain, and phenyl-methyl-carbinol and -ketone, together with 2,4-dihydroxy-ethylbenzene are formed (*Newitt*, *Burgoyme*, Proc. Roy. Soc. 153, 443).

(6) Alkyl phenols are obtained by the reduction of phenol-ketones with amalgamated zinc and HCl (*Clemmensen*, Ber. 47, 681).

(7) Phenol-carboxylic acids give phenols on destructive distillation of their salts with lime.

### Synthetic methods.

(8) When phenols and aliphatic alcohols are heated with  $\text{ZnCl}_2$  at 200°, hydrogen attached to the ring is replaced by alcohol residues (*Liebmann*, Ber. 14, 1842; *Auer*, Ber. 17, 669; *Baur*, Ber. 27, 1614; *Anschütz*, Ber. 28, 407).



At the same time, alkyl ethers of the phenols are formed. When methyl alcohol is used, the phenyl methyl ether,  $\text{PhOMe}$ , is the sole product. Magnesium chloride (Ber. 16, 792) and hydrogen alkali sulphates have a similar effect to zinc chloride (Ber. 16, 2541).

(9) Under the influence of conc. sulphuric acid, aluminium chloride, or boron trifluoride, unsaturated hydrocarbons, such as iso-amylene, add on phenols, and alkyl-phenols are formed (*Königs*, Ber. 25, 2649; Fr. Pat. 697,711). Propylene and *m*-cresol give several isomeric forms of isopropyl-*m*-cresol (see thymol, p. 190), and the corresponding saturated phenol ether.

(10) The introduction of alkyl groups into the nucleus of phenols by means of aluminium chloride, or ferric chloride (p. 38), is not, as a rule, a smooth reaction (cf. *Gurewitsch*, Ber. 32, 2424). The phenol ethers are more suitable. For the ethylation of phenol with ether and aluminium chloride see *Jannasch*, Ber. 32, 2391).

**Reactions.** *The replacement of hydrogen atoms.*—(1) Owing to their acidic nature the phenols readily form salts, especially with the alkalis. The hydrogen of the hydroxyl group is also easily replaced by (2) alkyl groups and (3) acyl groups. The esters formed with *p*-bromo- and *p*-nitro-benzoic acids, or the phenyl- and naphthyl-

urethanes (*Lyman*, *Am. Soc.* 42, 615) obtained with phenyl or  $\alpha$ -naphthyl isocyanate may be used for the identification of phenols.

(4) The substitution of nuclear hydrogen atoms by chlorine, bromine, and nitro-groups is facilitated by the presence of OH in the ring.

(5) The phenols combine with diazo- and azo-compounds with the formation of azo- and diazo-dyes (see hydroxy-azo compounds, p. 210).

(6) *Colour reactions of phenols.*—When a mono- or polyhydric phenol is added to a solution of 6 parts of potassium nitrite in 1 of conc. sulphuric acid intense colorations appear. Ordinary phenol gives first a brown, then a green, and finally a royal blue colour (Liebermann's reaction, *Ber.* 17, 1875). Indophenols are formed which dissolve in conc. sulphuric acid with a blue colour, and combine with alkalis to give cornflower-blue salts (*Decker*, *Ber.* 36, 2894). The phenols also give similar colours with diazo- and nitroso-compounds in the presence of sulphuric acid. Ferric chloride gives various colours with aqueous solutions of phenols, but alcoholic solutions of simple phenols do not give colours with this reagent. Mercuric nitrate containing a little nitrous acid gives a red colour with nearly all phenols (Plugge's reaction, *Ber.* 23, R 202).

*Replacement of the hydroxyl group.*—(7) When heated with zinc dust, phenols are converted into the corresponding hydrocarbons.

(8) The replacement of oxygen by chlorine by means of  $\text{PCl}_5$  does not occur readily in simple phenols; phenol itself gives  $\text{PhOPCl}_4$  (p. 196).  $\text{PCl}_5$  acts more readily on nitrophenols, when nitrochlorobenzenes are obtained.

(9) Phosphorus sulphide converts phenols into thiophenols. (10a) When heated with zinc chloride-ammonia the OH group is replaced by  $\text{NH}_2$  and aniline is formed (p. 72). (10b) Amino compounds are also produced when alkyl ethers of nitrophenols are heated with alcoholic ammonia. The reaction recalls the substitution of the O-alkyl group of esters by  $\text{NH}_2$ . (11) For the oxidation of the alkyl residue in homologous phenols see p. 188.

*Nuclear syntheses.*—(1) See methods (8), (9), and (10) above for the substitution of aromatic hydrogen atoms in phenols by alkyl groups. This substitution takes place with particular ease when unsaturated radicals are introduced; the benzyl group also enters readily even in an undissociated medium, preferably in the *o*-position (*Claissen*, *Angew.* 36, 478).

(2) The alkali salts of phenols combine with carbon dioxide at high temperatures to form alkali salts of hydroxy-acids, the *phenol carboxylic acids* (cf. salicylic acid). Sodium phenates combine with aliphatic olefine oxides to form glycol-aryl ethers (*Boyd*, *J.* 105, 2117).

(3) *Phenol carboxylic acids* are also obtained by the action on phenols of carbon tetrachloride and sodium hydroxide, and (4) hydroxy-aldehydes or *phenol aldehydes* are obtained by the action on phenols of chloroform and sodium hydroxide (see salicylaldehyde).

(5) Phenols condense with formaldehyde to give *phenol-alcohols*, such as saligenin. In the presence of acids or alkalis resinous condensation products are formed, which are more or less soluble in organic solvents. This process has been developed industrially by *Bakeland* (*Ind. Eng. Chem.* 5, 506; 17, 225, and numerous patents). The first product of alkaline condensation called *Bakelite A* (or "Resol"), is a liquid soluble in the usual organic solvents, and changing on heating, with further condensation, into *Bakelite B* (or "Resitole"), a solid which swells in organic liquids. Further heating under

pressure produces a hard, infusible, insoluble product, *Bakelite C* (or "Resite"). All these products, but particularly the last, are extensively used in the varnish and plastic industries. *p,p'*-Dihydroxydiphenyl-methane is probably the primary condensation product (*Raschig*, *Angew.* **25**, 1947; *Chattaway*, *J.* **1933**, 699; *Ellis*, *Synthetic Resins*, New York, 1923; *Barry et al.*, *Natural and Synthetic Resins*, London, 1926; *Rahm*, *Plastic Moulding*, New York, 1933).

(6) When phenols are heated with malic and sulphuric acids, coumarins (*q.v.*) are formed. With  $\beta$ -keto-acids, *coumarins* or *chromones* (*q.v.*) are formed, depending on the condensation agent and the nature of the phenol. Sulphuric acid always gives coumarins, while phosphorus pentoxide gives coumarins with resorcinol, phloroglucinol, pyrogallol, and  $\alpha$ -naphthol, but chromones with other phenols (*Robertson*, *J.* **1931**, 2426). (?) With benzotrichloride,  $\text{PhCCl}_3$ , the phenols give dyes of the *aurin* series, derived from triphenylmethane,  $\text{CHPh}_3$ . With phthalic or *o*-sulphobenzoic anhydrides the phenols give *phthaleins*. *Naphthalic* (*q.v.*), succinic, and other dicarboxylic anhydrides react in a similar manner. (8) Certain phenols combine with strong organic acids, such as trichloroacetic acid and picric acid, or with pyridine, forming double compounds, some of which are crystalline (*Kendall*, *Am.* **38**, 1309; *Hatcher*, *Am.* **39**, 1939). For the addition of arylenes to phenols see *Niederl*, *Am.* **56**, 2412. For exchange reactions between phenols and deuterium or heavy water see *Münzberg*, *Z. angew.* **50**, 317.

*Reduction of phenols.*—When vapours of phenols are passed with an excess of hydrogen over finely divided nickel at  $215\text{--}230^\circ$ , they are reduced to hexahydrophenols (*Sabatier*, *Senderens*, *C.r.* **137**, 1025). Hexahydroketones are formed as intermediate products (*Ipatiev*, *Ber.* **40**, 1286; *Vavon*, *Bull.* **37**, 296).

By reduction of phenol with alternating current, cyclohexanone is produced (*Drechsel*, *J.* pr. **38**, 65).

*The benzene nucleus of the phenols is broken down* (p. 28).—(1) By oxidising them with permanganate, (2) by treating with chlorine and decomposing the chlorinated products with alkalis.

**Phenol**, *carbolic acid*,  $\text{C}_6\text{H}_5\text{OH}$ , m.p.  $41^\circ$  (*Leroux*, *Pharm. et Chim.* **20**, 1919), b.p.  $183^\circ$ ,  $d_0$  1.084. This compound is obtained from aniline, from benzene sulphonic acid, from the three hydroxybenzoic acids, *etc.*, by the methods described above. Combined with other substances it occurs in nature in *Castoreum* and in the urine of herbivorous animals.

Commercial phenol from coal-tar is a colourless, crystalline mass which slowly turns reddish in the air (*Bach*, *Ber.* **27**, R 790; *Gibbs*, *Philippine J.* **1909**). Very pure phenol crystallises in long, colourless prisms. It has a characteristic smell, a strong burning taste, and is poisonous and antiseptic. It dissolves in 15 parts of water at  $20^\circ$ , and very readily in alcohol, ether, and acetic acid. It is volatile with steam. Its neutral solution gives a violet colour with ferric salts (*cf.* also Plugge's reaction, p. 186). Bromine water precipitates 2,4,6-tribromophenol even from very dilute solutions. When consumed by animals it appears in the urine as phenyl-glycuronic acid (*Vol. I*, p. 653) and as phenyl-sulphuric acid (p. 195).

When fused with caustic potash it is converted into diphenols,  $\text{C}_{12}\text{H}_8(\text{OH})_2$ , which are derivatives of diphenyl (p. 493). When distilled over lead monoxide

it forms diphenylene oxide. When heated with oxalic or formic acid and dehydrating agents, *aurin* (p. 542) is formed.

Potassium permanganate oxidises phenol to mesotartaric acid (Vol. I, p. 653). Permonosulphuric acid oxidises it to pyrocatechol and quinhydrone (p. 237) (*Bamberger*, J. pr. 68, 486). The final products of the action of chlorine are ketochlorides derived from di- and tetrahydrobenzenes (*Zincke*, Ber. 27, 537). Electrochemical oxidation gives catechol, hydroquinone, *o,p*- and *o,p'*-diphenol, quinone, and *o*-hydroxyphenyl ether (*Fichter*, Bull. 19, 281), and oxidation with hydrogen peroxide in the presence of ferrous sulphate gives largely catechol, pyrogallol, and other compounds (*Goldhammer*, Biochem. Z. 1927, 189). By the action of chlorine and sodium hydroxide phenol is converted into trichloro-cyclopentenedihydroxycarboxylic acid. The more important reactions of phenol have been mentioned above.

*History*.—Phenol was detected in coal-tar by *Runge* in 1834. He called it carbolic acid, and noted its physiological properties which resembled those of creosote (χαράς—*meal*, and σωζω—*preserve*). *Laurent* was the first to prepare pure phenol (1841). He called it “hydrate de phényle” or “acide phénique” from φαίνω—to shine, possibly because it was found in the tar produced in the preparation of illuminating gas. *Gerhardt* obtained it from salicylic acid and introduced the name “phenol” to indicate that the substance is an alcohol. *Lister*, of Glasgow, introduced it into surgery in 1867.

**PHENATES.** Potassium phenate and sodium phenate are prepared by dissolving phenol in caustic potash and soda, respectively, evaporating the solution, and rapidly drying the residue. Both compounds are readily soluble in water (Ber. 26, R 150). Carbon dioxide precipitates phenol from their aqueous solutions, phenol itself being insoluble in alkali carbonate solutions. For the action of carbon dioxide on dry phenates, see salicylic acid, p. 355. Nearly all the phenols form potassium-hydrogen salts of the type  $\text{PhOK} + m\text{PhOH} + n\text{H}_2\text{O}$ , but the corresponding sodium salts are unknown (*Meyer*, Z. anal. Chem. 64, 72). With formaldehyde and sulphuric acid they give a resinous product (see above).

**Calcium phenate**,  $(\text{PhO})_2\text{Ca}$ , and **mercuric phenate**,  $(\text{PhO})_2\text{Hg}$  are known. The compound  $\text{HO} \cdot \text{C}_6\text{H}_4\text{HgCl}$  is formed from phenol and mercuric chloride (p. 171). **Aluminium phenate**,  $(\text{PhO})_3\text{Al}$  is obtained as a vitreous mass, m.p. about  $265^\circ$ , when phenol is heated with aluminium (*Cook*, Am. 28, 608). The phenols combine with aluminium chloride and with nitrogenous bases (*Forcrand*, C.r. 116, 192; 128, 1519; *Perrier*, C.r. 122, 195; *Baeyer*, Ber. 35, 1207; *Ipatiev*, C. 1914, II, 1267).

### Homologous Phenols

It is a peculiarity of the cresols and other homologous phenols, that they cannot be oxidised by chromic acid. The OH group protects the alkyl group from oxidation by chromic acid. If, however, the phenolic hydrogen atom is replaced by alkyl or acyl radicals, as in the phenolic ethers and esters, the alkyl group is oxidised and ether- or ester-acids are formed. The sulphuric and phosphoric esters of the phenols are readily prepared and are easily oxidised by alkaline permanganate (*Heymann*, Ber. 19, 3304), while the free phenols would be destroyed by this reagent (cf. the oxidation of phenol, above). Under special conditions, the oxidation of the side-chain may stop at the aldehyde stage.

The sulphonie group in the homologous benzenesulphonic acids exerts a similar effect on the oxidisability of the alkyl groups. In general, negative atoms or groups of atoms in the *o*-position hinder the oxidation of alkyl groups by acidic oxidising

agents, and conversely, alkaline oxidising agents, such as potassium permanganate first attack the alkyl group in the *o*-position (Meyer, Ann. 220, 16).

The methyl groups of methyl-phenols, such as the cresols and xylenols, are oxidised to carboxyl groups by fusion with alkali hydroxides, best with the addition of lead monoxide or dioxide, and hydroxybenzoic, hydroxytoluic, hydroxyphthalic, etc., acids are formed (Grache, Ber. 39, 794; cf. the similar behaviour of homologous pyrroles and indoles, Vol. IV). *p*-Alkyl halogenophenols are oxidised by nitric acid to the so-called *quinitroles* and *quinols*. These substances are dealt with under "phenol alcohols" together with the *pseudo-phenol bromides* and *methylene quinones*. For other reactions, see p. 185.

The liquid homologous phenols are characterised by the melting points of their benzoyl esters and their phenylurethanes. These melting points will be given under each member.

1. **CRESOLS**, *hydroxytoluenes*,  $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$ . All the three isomers occur in coal-tar and in beech-wood tar. They are obtained from the toluidines by method (1), and from the toluene sulphonic acids by method (2) (p. 184). They smell like phenol, though rather less pleasantly, and they are less poisonous than phenol, but share its disinfecting properties. They are reduced by zinc dust to toluene when heated, and carbon dioxide and sodium converts them into cresotic acids. They behave towards fused potash and other oxidising agents as described above. For their condensation with acetone in the presence of acidic catalysts see Niedert, Mo. 60, 150. *o*-Cresol is obtained from carvacrol (p. 190), and *m*-cresol from thymol (p. 190). The latter is also obtained from the dibromide of synthetic 3-methyl-cyclohexenone (Vol. II, p. 115) by removal of  $2\text{HBr}$  (Knoevenagel, Ann. 281, 98).

*o*-Cresol, 1,2-*hydroxytoluene*, m.p.  $31^\circ$ , b.p.  $190^\circ$ , m.p. of the phenylurethane,  $141^\circ$ .

*m*-Cresol, 1,3-*hydroxytoluene*, m.p.  $11^\circ$ , b.p.  $202^\circ$ , m.p. of the phenylurethane,  $121$ – $122^\circ$ .

*p*-Cresol, 1,4-*hydroxytoluene*, m.p.  $37^\circ$ , b.p.  $201^\circ$ , m.p. of the phenylurethane,  $112$ – $113^\circ$ .

*o*-Cresol gives a blue colour with ferric chloride. The crude cresols are used as disinfectants; *creolin* is a solution of crude cresols in alkalis, *cresolin* is a solution of cresols in resin soaps, and *lysol* a solution in oily soap. For the reactions they undergo in the animal organism see Preusse, Ber. 14, 687. For the separation of *m*- and *p*-cresol, use may be made of the fact that the former is more readily sulphonated than the latter (Ger. Pat. 268,780), or the sulphonic acids may be fractionally decomposed by superheated steam (Brückner, Z. anal. Ch. 75, 289). For the freezing points of mixtures of phenol and each of the cresols see Dawson, J. 113, 923. For the ultraviolet absorption of the cresols see Savard, C.r. 188, 782.

2. **PHENOLS**,  $\text{C}_6\text{H}_5\text{OH}$ , *hydroxydimethyl-benzenes* and *hydroxyethyl-benzenes*. The six possible *xylenols*,  $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{OH}$ , have been prepared. The *ethyl-phenols*,  $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{OH}$ , have been obtained from the ethyl-benzene sulphonic acids (Behal, C.r. 118, 422).

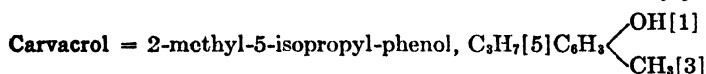
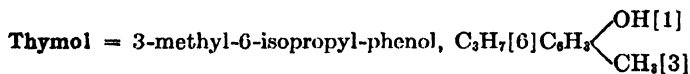
*o*-Ethyl-phenol, liquid, b.p.  $207^\circ$ ; benzoyl compound m.p.  $39^\circ$ .

*m*-Ethyl-phenol, m.p.  $-4^\circ$ , b.p.  $214^\circ$ ; benzoyl compound m.p.  $52^\circ$ .

*p*-Ethyl-phenol, m.p.  $46^\circ$ , b.p.  $218^\circ$ ; benzoyl compound m.p.  $59^\circ$ .

3. **PHENOLS**,  $\text{C}_8\text{H}_9\text{OH}$ , 2,4,6-*trimethyl-phenol*, *mesitol*,  $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{OH}$ , m.p.  $71^\circ$ , b.p.  $221^\circ$ , is obtained from aminomesitylene or from mesitylenic acid. It is oxidised by silver oxide to tetramethyl-stilbene-quinone (Goldschmidt, Ber. 56, 1963). 3,4,5-*Trimethyl-phenol*, *sym-hemimellitol*, m.p.  $81^\circ$ . 2,3,4-*Hemimellitol*, m.p.  $107^\circ$  (Auwers, Ber. 58, 2815). 2,4,5-*pseudo-Cumenol*,  $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{OH}$ , m.p.  $71^\circ$ , b.p.  $232^\circ$ , is obtained from *pseudo-cumene* sulphonic acid (Auwers, Ber. 17, 2976). For the products obtained by brominating it, and the formation of *pseudo-phenol bromides* insoluble in alkalis, see p. 198. 3-*n*-*Propyl-phenol*, b.p.  $220^\circ$  is obtained from isosafrol (Ciamician, Ber. 23, 1162). 4-*n*-*Propyl-phenol*, b.p.  $234^\circ$ . *p*-*Isopropyl-phenol*, *p-cumenol*, *australol*, occurs in the oil of *Eucalyptus polybractea* (Earl, J. New South Wales, 1926), m.p.  $21^\circ$ , b.p.  $229^\circ$ . It has been obtained, together with hydroquinone, by condensing acetone and phenol by means of fuming  $\text{HCl}$  to diphenol- $\beta$ -propane,  $(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$ , and fusing this with potash (Dianin, Ber. 25, R 334), and by allowing *p*-isopropyl-phenyl magnesium bromide to oxidise in the air (Bert, Bull. 37, 1397).

4. **PHENOLS**,  $C_{10}H_{18}OH$ . Two of these phenols, **thymol** and **carvacrol**, occur in a number of essential oils. Both are methyl-propyl phenols of which twenty isomers are possible, and since both are derivatives of the common *p*-cymene, they must contain an isopropyl radical. When heated with phosphorus pentoxide thymol decomposes into propylene and *m*-cresol, and carvacrol into propylene and *o*-cresol. Hence:



**Thymol**, m.p.  $51^\circ$ , b.p.  $232^\circ$ , crystallises in large, colourless plates. It is found, together with cymene, in oil of thyme from *Thymus vulgaris*, and in the oils from *Ptychotis ajowan* and *Monarda punctata*. To isolate it the oils are shaken with caustic potash, the liquid filtered, and the thymol precipitated by the addition of acid. Thymol is obtained artificially from nitrocuminic aldehyde (p. 270), and from dibromomenthone (Vol. II, p. 231) by removal of hydrogen bromide (*Beckmann*, Ber. 29, 420). It is also obtained from umbellulone (Vol. II, p. 245). Industrially, the extraction of ajowan seed is not now used. Thymol is made by oxidising piperitone,  $\Delta^2$ -menthenone-3 (Vol. II, p. 233) with ferric chloride, or synthetically by introducing the isopropyl radical into *m*-cresol. This can be done (1) by thermal rearrangement of *m*-cresol isopropyl ether; (2) by condensing *m*-cresol and acetone under suitable conditions (heating under pressure, etc.) and hydrogenating the product (*Zincke*, Ann. 388, 299; Br. Pats. 273,684/5, 308,741, and 344,970); (3) by treating *m*-cresol with propylene or agents which give propylene, e.g., (iso-) propyl alcohol and sulphuric acid or zinc chloride, subsequently eliminating the sulphonic group (if sulphuric acid is used) (Ger. Pats. 350,809 and 379,952; Br. Pat. 270,283, etc.; Sw. Pats. 142,738 and 144,206; U. S. Pats. 1,788,847, 1,798,813, and 1,805,555). In these reactions, two isomers of thymol, m.p.  $69^\circ$  and  $114^\circ$ , are formed as by-products. Both can be converted into thymol. U. S. Patents 1,378,939 and 1,449,121 start from cymene, which is either nitrated in the 2-position, reduced to the amine, diazotised, and boiled with water, or sulphonated in the 2-position and then fused with alkali. Thymol has a powerful odour of thyme. It is an antiseptic.

When distilled with phosphorus pentasulphide it is converted into cymene; when oxidised it gives *thymoquinone* (p. 238). Iodine and caustic alkali converts it into diiodo-dithymol, 3,3'-diiodo-2,2'-dimethyl-5,5'-diisopropyl-diphenoquinone-4,4' (Ar. Pharm. 272, 8). This is known as *aristol* or *annidaline* in medicine, where it is used as a substitute for iodoform. For the mechanism of bromination and iodination of thymol see *Dannenberg*, Mo. 24, 67.

**Carvacrol**, m.p.  $1^\circ$ , b.p.  $236^\circ$ , is isomeric with thymol. It occurs in the combined state in the oil of some species of *Satureja* and *origanum*, e.g., in *Satureja hortensis* and in *Origanum hirtum*. It is obtained from the isomeric *carvone*, a derivative of dihydrocymene (Vol. II, p. 237), which occurs in cumin oil (from *Carum carvi*) and

some other essential oils, by heating with crystalline phosphoric acid. Carvacrol is also obtained when camphor is heated with one-fifth of its weight of iodine under reflux. It is synthesised from cymene-sulphonic acid (*Jacobsen*, Ber. 11, 1060; U. S. Pat. 1,449,121). For the preparation of the pure compound see *John J.* pr. 143, 253. When distilled with phosphorus pentasulphide it gives cymene and thiocarvacrol,  $C_{11}H_{13}SH$  (p. 214).

*sym*-Carvacrol,  $(CH_3)[3](CH_3)_2CH[5]C_6H_3[1]OH$ , m.p.  $54^\circ$ , b.p.  $241^\circ$  (Ber. 27, 2347). *o*-Methyl-*m-n*-propyl-phenol,  $(CH_3)[2]C_6H_7[5]C_6H_4[1]OH$ , b.p.  $240^\circ$ , is obtained from the corresponding sulphonic acid (Ber. 29, R 417). *p*-tert.-Butyl-phenol,  $(CH_3)_3C[4]C_6H_4[1]OH$ , m.p.  $98^\circ$ , b.p.  $237^\circ$ , obtained from isobutyl alcohol, phenol, and zinc chloride (*Senkowsky*, Ber. 24, 2974) gives trimethylpyruvic and trimethylacetic acids on oxidation with potassium permanganate (*Anschütz*, Ann. 327, 201).

*p*-Isoamyl-phenol,  $(CH_3)_2CH(CH_2)_2[4]C_6H_4[1]OH$ , b.p.  $261-262^\circ$ ; *p*-tert.-amyl-phenol,  $(CH_3)_2(C_2H_5)C[4]C_6H_4[1]OH$ , m.p.  $93^\circ$ , b.p.  $255^\circ$  (*Claisen*, unpub.) is obtained from phenol, isoamyl or tertiary amyl alcohol and zinc chloride, or from isoamylene, acetic acid and sulphuric acid (*Anschütz*, Ber. 28, 407). When oxidised with potassium permanganate it gives dimethyl-ethyl-pyruvic acid and dimethyl-ethyl acetic acid (*Anschütz*, Ann. 327, 201).

Tetramethyl-phenols (*Jacobsen*, Ber. 15, 1854; 18, 2842; *Limpach*, Ber. 21, 645; *Tohl*, Ber. 21, 907). Pentamethyl-phenol, m.p.  $126^\circ$ , b.p.  $267^\circ$  (*Hofmann*, Ber. 18, 1826). Diethyl-phenols, tetra-ethyl-phenol (*Voswinckel*, Ber. 22, 317).

*m*-Pentadecyl-phenyl, *hydrojaukgot*, m.p.  $50^\circ$ , has been obtained from the methyl ether of *m*-methoxyphenyl-tetradecyl-ketone by *Clemmensen's* method (*Furukawa*, Chem. Res. 24, 320).

2-Benzyl-4-methyl-phenol, m.p.  $35-36^\circ$ , is obtained from benzyl alcohol and *p*-cresol by the action of aluminium chloride, or from sodium *p*-cresolate and benzyl chloride, with subsequent rearrangement. A by-product of the first reaction is 2,6-dibenzyl-4-methyl-phenol, b.p.  $236-238^\circ$  (8 mm.) (*Huston*, Am. 53, 2379).

### Functional Derivatives of Monohydric Phenols.

The reactions of the phenols will be illustrated by taking phenol itself as an example, as the substance is readily available and its reactions have been studied in greater detail than those of any of its homologues. In those cases where derivatives of a homologous phenol are of special theoretical or practical interest they will be mentioned after the corresponding phenol derivative.

**PHENOLIC ETHERS.** (1) The phenol ethers are formed by the action of alkyl halides on phenates in the same way as the ethers of the aliphatic alcohols. The phenol is heated with caustic potash and alkyl iodide, or methyl chloride is passed over sodium phenate at  $200^\circ$  (*Vincent*, Ber. 16, 2513), preferably under pressure (U. S. Pat. 1,801,901).

Other methods of formation are (2) by the action of alkyl sulphates on alkali phenates in water or alcohol (*Gladstone*, J. 99, 25); (3) by the decomposition of benzene diazonium compounds with alcohols, when hydrocarbons are formed at the same time (*Hirsch*, Ber. 25, 1973); (4) by heating methyl phenylcarbonate (p. 196) when carbon dioxide is eliminated:  $PhOCOCH_3 = PhOCH_3 + CO_2$  (*Einhorn*, Ber. 42, 2237).

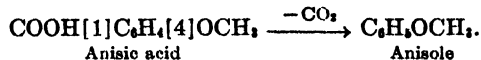
(5) Diazomethane in the cold converts phenols into their methyl ethers, nitrogen being evolved (*Pechmann*, Ber. 28, 857).





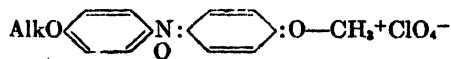
Industrially, dimethyl sulphate,  $(\text{CH}_3)_2\text{SO}_4$ , diethyl sulphate,  $(\text{C}_2\text{H}_5)_2\text{SO}_4$ , *p*-toluene sulphonic ester (p. 175), etc., are used on a large scale for alkylating phenols (Ullmann, Ann. 327, 120; Ger. Pat. 76,574).

(6) By heating the alkyl ethers of phenol-carboxylic acids with lime or baryta:



(7) By passing the vapours of phenols and alcohols together over thoria heated to  $420^\circ$  (Mailhe, Chem. Z. 35, 485). (8) Olefines combine with phenols in the presence of sulphuric or phosphoric acids to form phenyl-alkyl ethers. By a secondary reaction these partially rearrange to give alkyl-phenols. The latter boil at a much higher temperature than the former (Niedert, Natelson, Am. 53, 1928; Tshitshibabin, C.r. 198, 1239; U. S. Pat. 1,948,287). (9) Phenyl-ether ketones are reduced by Clemmensen's method, with amalgamated zinc and hydrochloric acid. The method is analogous to that used in the preparation of phenols (p. 185) (Johnson, Am. 35, 1014). (10) Phenates and alcohols are treated with CO (Zerbe, Brennstoff-Chem. 16, 88).

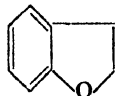
The phenol ethers are unaffected by boiling with alkalis, but prolonged heating with alcoholic potash at high temperatures decomposes them with the formation of phenols (Stoermer, Ber. 34, 1812). Ethers of polyhydric phenols are partially hydrolysed by the same treatment, veratrol, for example, being converted into guaiacol (p. 219) (C. 1898, I, 456). The phenol ethers will combine with oxygen acids ( $\text{HNO}_3$ ,  $\text{HClO}_4$ ) to give oxonium salts (Kehrmann, Ber. 52, 2119). When heated with the halogen acids they usually decompose:  $\text{PhOMe} + \text{HI} = \text{PhOH} + \text{MeI}$ . A quantitative method of estimating the number of methoxy and ethoxy groups present in a compound is based on the ease of decomposition of the phenol alkyl ethers by concentrated hydriodic acid. The methyl or ethyl iodide formed is passed into an alcoholic solution of silver nitrate and the silver iodide precipitated is collected and weighed (Zeisel, Mo. 6, 989; 7, 406), or the alkyl iodides are absorbed in a solution of bromine and potassium acetate in glacial acetic acid, when their iodine is converted into iodic acid. The latter is estimated iodometrically, after eliminating the excess of bromine with formic acid (Vieboeck, Ber. 63, 2818). Aniline hydrochloride (Klemenc, Ber. 49, 1371), aluminium chloride, and particularly aluminium bromide (Hartmann, Ber. 25, 3531), also decompose the phenol ethers. Phosphorus pentachloride chlorinates the nucleus, but does not break the ether linkage (Authenrieth, Ber. 28, R 612). For other demethylating agents, see Takagi, J. Pharm. Japan, 1925. For the decomposition of phenol ethers by organo-magnesium compounds see Grignard, Bull. [5], 3, 1181. Towards chlorine, bromine, iodine, nitric acid, and sulphuric acid, the phenol ethers behave like aromatic hydrocarbons. The halogenation of phenol ethers has been studied in detail, and the rate of the reaction has been measured by Bradfield, Jones, and Orton, J. 1929, 2810; 1931, 2903. When phenol ethers are nitrated intensely coloured solutions are produced, from which crystalline compounds can be obtained by the addition of aqueous perchloric acid. They are probably formulated as follows:



**Anisole, phenyl methyl ether**,  $\text{PhOMe}$ , b.p.  $152^\circ$ ,  $d_4^{20}$  0.991, is obtained from anisic, or *p*-methoxybenzoic acid (p. 363). A method of preparing it from phenol, dimethyl sulphate, and sodium hydroxide is described by *Hiers and Hager, Org. Synth.* 9, 12. For its behaviour on distillation with zinc dust, see *Thoms, Arch. Pharm.* 242, 95. For the reaction when heated with Grignard reagents see *Simonis, Ber.* 47, 269.

**Phenetole, phenyl ethyl ether**,  $\text{PhOEt}$ , m.p.  $-30.2^\circ$ , b.p.  $172^\circ$ ,  $d_4^{20}$  0.9822, dipole moment 1.2 D. **Isoamyl phenyl ether**, b.p.  $225^\circ$ . **Bromoethyl phenyl ether**,  $\text{BrCH}_2\cdot\text{CH}_2\cdot\text{OPh}$ , m.p.  $39^\circ$  (*Weidige, J. pr.* 24, 242), is converted by

zinc chloride into coumaran,



, ring closure taking place (*Rindfuss, Am.*

41, 665).

**PHENYL OLEFINE ETHERS.** **Phenyl-vinyl ether**,  $\text{PhOCH}:\text{CH}_2$ , b.p.  $155-156^\circ$ , is obtained by the action of solid sodium hydroxide on phenyl- $\beta$ -bromoethyl ether (*Powell, Am.* 42, 646), or by the action of bases on phenol and vinyl chloride (Ger. Pat. 513,679), or by the action of alcoholic sodium hydroxide on phenol and ethylene chloride or ethylidene chloride (Ger. Pat. 525,188). On heating it gives phenol and acetaldehyde-diphenyl acetal,  $\text{CH}_3\text{CH}(\text{OPh})_2$ , m.p.  $9^\circ$ , b.p.  $154^\circ$  (14 mm.) (*Lauer, Am.* 55, 1572). **Phenyl- $\omega$ -bromovinyl ether**,  $\text{PhOCH}:\text{CHBr}$ , b.p.  $116^\circ$  (15 mm.), obtained from potassium phenate and acetylene dibromide, gives with alcoholic potash, **phenoxy-acetylene**,  $\text{PhOC}:\text{CH}$ , b.p.  $75^\circ$  (35 mm.), an unstable oil, which readily forms normal acetylene salts, such as  $\text{PhOC}:\text{CNa}$ ,  $\text{PhOC}:\text{CAG}$ ,  $(\text{PhOC}:\text{C})_2\text{Cu}_2$  (*Slimmer, Ber.* 36, 289). **Phenoxy-propine**,  $\text{PhOCH}_2\text{C}:\text{CH}$ , b.p.  $98^\circ$  (23 mm.) is obtained by the action of sodium on phenyl- $\gamma$ -chloroallyl ether (*Bert, C.r.* 194, 886).

**Phenyl-allyl ether**,  $\text{PhOCH}_2\text{CH}:\text{CH}_2$ , b.p.  $73^\circ$  (11 mm.), b.p.  $191-192^\circ$ , is prepared from phenol and allyl bromide under the action of potassium carbonate in acetone solution, on a water bath. It is an oil with a strong odour of geraniums. When it is boiled for several hours at ordinary pressure with a current of carbon dioxide passing through it, the boiling temperature gradually rises to  $220^\circ$ . By a rearrangement, first observed by *Claisen* (Ber. 45, 3157; Ann. 418, 210; 442, 410), *o*-allyl-phenol,  $\text{HO}[2]\text{C}_6\text{H}_4\text{CH}_2\text{CH}:\text{CH}_2$  (p. 450) is formed, together

with a small amount of the isomeric 2-methyl-coumaran,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}\rangle\text{CH}:\text{CH}_2$

(Vol. IV). This rearrangement takes place to a certain extent in the preparation of phenyl-allyl ether, especially if the reaction is carried out in a non-dissociating solvent. By re-treating *o*-allyl-phenol with allyl bromide and potassium carbonate, *o*-allyl-phenol-allyl ether b.p.  $104-105^\circ$  (10 mm.) is obtained, and if this is heated for some time, *o,o*-diallyl-phenol (p. 450) is formed. Repeating the same treatment a third time, another allyl ether and finally *o,o,p*-triallyl-phenol are formed. More than three allyl groups cannot be introduced into the benzene nucleus by this method. In this rearrangement, the allyl group first enters the *o*-position with reference to the phenol oxygen, and only when both ortho positions are occupied does it go into the para-position if this be free.

The mechanism of this rearrangement has been followed by examining what happens with higher phenol ethers of the type  $\text{PhOCH}(\text{Alk})\cdot\text{CH}:\text{CHCH}_3$ . Contrary to expectation, it is not the  $\alpha$ -C atom of the allyl group (the one which is linked to the phenol oxygen) which enters the nucleus, but the  $\gamma$ -C atom from the end of the chain migrates while the double bond shifts from the  $\beta,\gamma$ -into the  $\alpha,\beta$ -position. A phenol ether of the above type becomes a phenol of the formula  $\text{HO}\cdot\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}:\text{CH}(\text{Alk})$  (*Claisen, Ber.* 58, 275; 59, 2344; *Hurd, Am.* 53, 1917). The allyl group is inverted in the course of this rearrangement, and the reaction is closely connected with the structure of this group, since other unsaturated groups, e.g., those in phenyl- $\Delta^3$ -butenyl ether,  $\text{PhOCH}_2\text{CH}_2\text{CH}:\text{CH}_2$ , b.p.  $209^\circ$ , or in phenyl-vinyl ether, do not migrate into the nucleus (*Powell, Am.* 42, 646). Similarly the  $\alpha$ -ethyl ether,  $\text{PhO}\cdot\text{CH}(\text{C}_2\text{H}_5)\text{CH}:\text{CH}_2$ , rearranges in the normal way to  $\text{HO}[2]\text{C}_6\text{H}_4[1]\text{CH}_2\text{CH}:\text{CHCH}_2\text{C}_2\text{H}_5$ , but the  $\gamma$ -ethyl ether,  $\text{PhO}\cdot\text{CH}_2\text{CH}:\text{CHCH}_2\text{C}_2\text{H}_5$ , somewhat surprisingly undergoes a rearrangement into  $\text{HO}[2]\text{C}_6\text{H}_4[1]\text{CH}(\text{CH}_3)\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$ , as proved by its oxida-

tion to the corresponding phenoxy-acetic acid and conversion into a dicarboxylic acid (*Lauer, Filbert, Am. 58, 1388*). Again, phenyl-cinnamyl ether  $\text{Ph} \cdot \text{O} \cdot \text{CH} : \text{CHPh}$  gives *o*-( $\alpha$ -phenylallyl)-phenol,  $\text{HO}[2]\text{C}_6\text{H}_4[1]\text{CH}(\text{Ph}) \cdot \text{CH} : \text{CH}_2$ . In the rearrangement of phenyl-allyl ether, *o*-allyl-phenol is formed together with a dimer, *o*-(2-allyl-phenoxypropyl)-phenol,  $\text{HO}[2]\text{C}_6\text{H}_4[1]\text{CH}_2 \cdot \text{CH}(\text{CH}_2) \cdot \text{O}[2']\text{C}_6\text{H}_4[1']\text{CH}_2 \cdot \text{CH} : \text{CH}_2$ . This is an oil almost insoluble in 20 per cent caustic potash (*Hurd, Schmerling, Am. 59, 107*). For an analogous reaction, the formation of *o*- and *p*-alkyl phenols from phenyl-alkyl ethers by means of aluminium chloride, see *Smith, Am. 56, 717, 1419*. For phenyl-benzyl ethers see *Behagel, Ber. 67, 1368*. Phenyl ethers of the general formula  $(\text{PhO})(\text{CH}_2)_n\text{CH} : \text{CH}_2$ , see *Braun, Ber. 45, 1246*.

**Aryl- $\omega$ -chloroallyl ethers**,  $\text{Ar} \cdot \text{OCH}_2\text{CH} : \text{CHCl}$ , are prepared from phenols and 1,3-dichloropropene in the presence of sodium ethylate. **Phenyl-chloroallyl ether**, b.p.  $120^\circ$  (20 mm.); *o*-, *m*-, *p*-cresyl-allyl ethers, see *Bert, C.r. 192, 1565*. Those phenol ethers which contain halogen in the allyl group behave irregularly as regards the Claisen rearrangement (*Hurd, Webb, Am. 58, 2190*).

**Phenyl-isopropenyl ether**,  $\text{PhOCH}(\text{CH}_3) : \text{CH}_2$ , b.p.  $169^\circ$ , obtained from potassium phenate and isopropenyl bromide, isomerises when boiled with acetic acid and some sulphuric acid into *o*-isopropenyl phenol, b.p.  $213^\circ$ , passing through several intermediate stages. For details of this reaction see *Niederl, Am. 55, 284*.

**Phenyl-methylene ether**,  $\text{CH}_2(\text{OPh})_2$ , m.p.  $81^\circ$ , b.p.  $165^\circ$  (*Bischoff, Ber. 40, 2789*). **Phenyl-ethylene ether**, glycol-diphenyl ether,  $\text{PhOCH}_2\text{CH}_2\text{OPh}$ , m.p.  $95^\circ$ , is isomeric with phenol acetal,  $(\text{PhO})_2\text{CHCH}_3$ , m.p.  $10^\circ$ , b.p.  $175^\circ$ , obtained from potassium phenate and aldehyde chloride (*Fosse, C.r. 130, 725*). **Glycol-monophenyl ether**, b.p.  $165^\circ$  (80 mm.).  **$\gamma$ -Hydroxypropyl-phenyl ether**,  $\text{PhO}(\text{CH}_2)_2\text{CH}_2\text{OH}$ , b.p.  $158\text{--}160^\circ$  (25 mm.), is obtained from trimethylene chlorhydrin and phenol under the influence of sodium ethylate. When acted upon by

zinc chloride, ring closure occurs and *chroman*, , is formed (*Rindfuss,*

*Am. 41, 665*). **Glycerol-monophenyl ether**,  $\text{PhOCH}_2 \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}$ , m.p.  $70^\circ$ , is prepared by heating phenol with glycerol and a little sodium acetate

(*Zivkovic, Mo. 29, 951*), or by hydrating phenyl-glycide ether,  $\text{PhOCH}_2 \cdot \text{CH} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{CH}_2$ , b.p.  $242^\circ$ . The latter is obtained by the interaction of sodium phenate and epichlorhydrin. **Glycerol-diphenyl ether**,  $\text{PhOCH}_2 \cdot \text{CHOH} \cdot \text{CH}_2\text{OPh}$ , m.p.  $82^\circ$  is also formed at the same time (*Boyd, J. 93, 838; Fourneau, Pharm. chimie 1910*). **4-Ethyl-anisole**, b.p.  $195\text{--}198^\circ$ , is prepared by reducing *p*-acetyl-anisole with amalgamated zinc and hydrochloric acid (*Johnson, Am. 35, 1014*).

**PHENOXY-ALKYLAMINES.**  **$\beta$ -Phenoxy-ethylamine**,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OPh}$ , b.p.  $228^\circ$  (*Schreiber, Ber. 24, 189*).  **$\gamma$ -Phenoxy-propylamine**,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OPh}$ , b.p.  $241^\circ$  (*Lohmann, Ber. 24, 2637*).  **$\delta$ -Phenoxy-butylamine**,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OPh}$ , b.p.  $255^\circ$  (*Gabriel, Ber. 24, 3232*).

**PHENOL ETHERS OF ALDEHYDE-ALCOHOLS, KETO-ALCOHOLS, AND HYDROXY-ACIDS.** These are obtained from the corresponding chloro-aldehydes, -ketones, and -carboxylic acids by the action of sodium phenate. **Phenoxy-acetaldehyde**,  $\text{PhO} \cdot \text{CH}_2\text{CHO}$ , b.p.  $119^\circ$  (30 mm.); (*Pomeranz, Ber. 28, R 295*); **phenoxy-acetone**,  $\text{PhOCH}_2\text{COCH}_3$ , b.p.  $230^\circ$ , condenses with conc. sulphuric acid to methyl-coumarone (*Stoermer, Ber. 28, 1253; 35, 3553*). **Phenoxy-acetic acid**,  $\text{PhOCH}_2\text{COOH}$ , m.p.  $96^\circ$ , isomeric with mandelic acid,  $\text{PhCH}(\text{OH})\text{COOH}$ , is obtained by the action of monochloroacetic acid on potassium phenate at  $150^\circ$ , and by oxidation of phenoxy-acetaldehyde. It is a powerful antiseptic (*Hantzsch, Ber. 19, 1296; Auwers, Ber. 27, 2796*). **Phenoxy-acetyl chloride**,  $\text{PhOCH}_2\text{COCl}$ , b.p.  $169^\circ$  (60 mm.) (*Stoermer, Ber. 35, 3560*). **Di-phenoxy-acetic acid**,  $(\text{PhO})_2\text{CHCOOH}$ , m.p.  $91^\circ$  (*Auwers, Ber. 27, 2796*).  **$\alpha$ - and  $\gamma$ -Phenoxy-butyric acids**, m.p.  $99^\circ$  and  $60^\circ$  (*Luchmann, Ber. 29, 1421*). Homologous  $\alpha$ -phenoxy-fatty acids, see *Bischoff, Ber. 33, 924, 1249*.

**$\alpha$ -Phenoxy-acetoacetic ester**,  $\text{CH}_3\text{CO} \cdot \text{CH}(\text{OPh})\text{COOC}_2\text{H}_5$ , obtained from sodium phenate and  $\alpha$ -chloroacetoacetic ester, is a thick oil, which condenses under the influence of conc. sulphuric acid to *methyl-coumarilic ester*. **Phenoxy-fumaric ester**,  $\text{PhOC}(\text{COOR}) : \text{CHCOOR}$ , is obtained from sodium phenate and acetylene

dicarboxylic ester (*Pomeranz*, *Mo.* 15, 739). Cresoxy- and xylenoxy-acetic acids have been used for separating isomeric phenols (*Glund*, *C.* 1919, I, 626).

**PHENYL ETHERS.** (Di-)phenyl ether, diphenyl oxide,  $\text{Ph}_2\text{O}$ , m.p. 28°, b.p. 252°, dipole moment 1.1 D., crystallises in long needles and has an odour of geraniums. It is obtained by distilling copper benzoate, phenyl benzoate being a by-product. It is also obtained by heating a mixture of benzene diazonium sulphate and phenol (*Hirsch*, *Ber.* 25, 1973), or by heating phenol with zinc chloride, or better, aluminium chloride, to 350° (*Merz*, *Ber.* 14, 189). It is prepared very smoothly by heating potassium phenate with phenyl halides in the presence of copper bronze (*Ullmann*, *Ann.* 350, 83), or by heating potassium phenate with an aqueous suspension of calcium or barium oxides to 250–300° (U. S. Pat. 1,744,961), or by dehydrogenating phenol at 450° with thorium oxide as a catalyst (*Bruner*, *Helv.* 15, 619). Phenyl nitro-halides react with potassium phenate even in the absence of copper. When a mixture of phenol oxide and hydrogen is passed over finely divided nickel at 250°, the former is decomposed into benzene and phenol, with subsequent hydrogenation of these products to hexahydrophenol and cyclohexane (*Mailhe*, *Bull.* 11, 122).

**PHENOL ESTERS. ACID ESTERS OF PHENOL** are obtained by acting on phenols or their salts with acid chlorides or anhydrides, and by digesting phenols with acids and phosphorus oxychloride. In polyhydric phenols all the hydroxylic hydrogen atoms can be replaced by acetyl by treating a solution of the phenol in dilute alkali with acetic anhydride (*Chattaway*, *J.* 1931, 2495). Like all esters, the phenol esters are hydrolysed into their components when boiled with alkalis or even with water.

**ESTERS OF INORGANIC ACIDS.** *Phenyl sulphurous acid*, is not known in the free state. Its sodium salt,  $\text{NaSO}_2\text{OPh}$ , is formed by the action of sulphur dioxide on sodium phenate. Methyl iodide converts it into phenyl methylsulphonate,  $\text{MeSO}_2\text{OPh}$ . Salts of aryl sulphonic esters are also formed by the action of sodium bisulphite on phenols. They are very reactive, and in some the  $\text{OSO}_2\text{Na}$  group is replaced by  $\text{NH}_2$  on heating with ammonia (*Ger. Pat.* 115,335). The ester of sulphurous acid, diphenyl sulphite,  $\text{SO}(\text{OPh})_2$ , b.p. 185° (15 mm.), has been obtained by *Richter* (*Ber.* 49, 2339) from phenol, thionyl chloride and pyridine in carbon disulphide solution. For phenyl esters of methionic acid,  $\text{CH}_2(\text{SO}_3\text{H})_2$ , and of homologous acids, see *Schroeter*, *Ann.* 418, 161.

**PHENYL SULPHURIC ACID**,  $\text{PhO} \cdot \text{SO}_3\text{H}$ , is not known in the free state, when liberated from its salts by concentrated hydrochloric acid it immediately decomposes into phenol and sulphuric acid. Its potassium salt,  $\text{PhO} \cdot \text{SO}_3\text{K}$ , crystallises in leaflets, and is not very soluble in cold water. It occurs in the urine of herbivorous animals, and also in that of man and the dog after ingestion of phenol. It is prepared synthetically by heating potassium phenate with an aqueous solution of potassium pyrosulphate (*Baumann*, *Ber.* 9, 1715; *Czapek*, *Mo.* 35, 635); or by the action of sulphuryl chloride,  $\text{SO}_2\text{Cl}_2$ , on benzene solutions of alkali phenates (*Battegay*, *C.r.* 194, 1505). It can also be obtained from phenol and chlorosulphonic acid with pyridine in carbon disulphide, and subsequent treatment of the product with caustic potash. The phenyl-sulphuric acids are stable in neutral and alkaline solution, but are rapidly decomposed on heating with mineral acids. If potassium phenylsulphate is heated in a tube it passes smoothly into potassium *p*-phenol sulphonate.

**PHENYL ESTERS OF THE PHOSPHORIC ACIDS.** These are produced by the action of phosphorus trichloride and phosphorus oxychloride on phenol (*Anschtütz*, *Ann.* 239, 310; 253, 120; *Ber.* 30, 2396):

Phenyl-phosphorous chloride,  $\text{C}_6\text{H}_5\text{O} \cdot \text{PCl}_2$ , b.p. 90° (11 mm.)

Diphenyl-phosphorous chloride,  $(\text{C}_6\text{H}_5\text{O})_2\text{PCl}$ , b.p. 172° (11 mm.)

Triphenyl phosphite,  $(\text{C}_6\text{H}_5\text{O})_3\text{P}$ , b.p. 220° (11 mm.)

Phenyl-phosphoric chloride,  $(\text{C}_6\text{H}_5\text{O})\text{POCl}_2$ , b.p. 121° (11 mm.)

Diphenyl-phosphoric chloride,  $(\text{C}_6\text{H}_5\text{O})_2\text{POCl}$ , b.p. 195° (14 mm.)

Monophenyl phosphate,  $(\text{C}_6\text{H}_5\text{O})\text{PO}(\text{OH})_2$ , m.p. 99.5°

Diphenyl phosphate,  $(\text{C}_6\text{H}_5\text{O})_2\text{POOH}$ , m.p. 70°, hydrate (+2H<sub>2</sub>O), m.p. 51°

Triphenyl phosphate,  $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ , m.p. 49°, b.p. 245° (14 mm.)

Triphenyl phosphoric acid dichloride,  $(\text{C}_6\text{H}_5\text{O})_3\text{PCl}_2$ , decomp. 200–210°.

The mono- and di-phosphates are prepared by decomposing the corresponding chlorides with water. Triphenyl phosphate, however, is best prepared by shaking an alkaline solution of phenol with phosphorus oxychloride. The mono- and di-

phosphates add on chlorine to form phenyl-phosphoric tetrachloride,  $C_6H_5OPCl_4$ , and diphenyl-phosphoric trichloride,  $(C_6H_5O)_2PCl_3$ , respectively. Triphenyl phosphate is used considerably as a softening agent. For the reactions of phenoxy-phosphorus chlorides with water, alcohol, phenols, etc., see *Anschütz*, Ann. 525, 309.

**PHENOL SULPHOPHOSPHATES**, e.g., triphenyl sulphophosphate,  $(PhO)_3PS$ , m.p.  $53^\circ$  (*Authenrieth*, Ber. 31, 1094).

**PHENYL SILICATES**, see *Hertkorn*, Ber. 18, 1679.

**PHENYL CARBONATES**. Free phenyl-carbonic acid is unknown, but sodium phenyl-carbonate, a white powder, decomposed by water has been obtained by acting upon sodium phenate with carbon dioxide, preferably under pressure. When it is heated, under pressure, at  $120-130^\circ$ , it rearranges to *sodio-phenol-o-carboxylic acid*,  $NaOC_6H_4COOH$ , a reaction recalling the rearrangement of phenyl-sulphuric into phenol-sulphonic acid. Sodium phenyl-carbonate and sodium phenate give disodium salicylate and phenol on heating to  $190^\circ$  (*Tijmstratz*, Ber. 38, 1375).

Phenyl carbonate,  $CO(OPh)_2$ , m.p.  $80^\circ$ , b.p.  $168^\circ$  (15 mm.) is produced when phenol and phosgene gas,  $COCl_2$ , are heated to  $150^\circ$ , or more readily by passing phosgene into an aqueous solution of sodium phenate (*Bischoff*, Ber. 35, 3434). It is also obtained by boiling phenol and carbon tetrachloride with a mixture of zinc oxide and zinc chloride (*Gomberg*, Am. 47, 198). In this reaction dichlorodiphenoxy-methane,  $CCl_2(OPh)_2$ , is an intermediate product, and changes, unless zinc oxide be added, into the two isomeric dichloro-di-*o,o'*- and *o,p'*-hydroxyphenyl-methanes,  $CCl_2(C_6H_4OH)_2$ , which are further hydrolysed to dihydroxybenzophenones (p. 521). It crystallises from alcohol in shining needles. When heated with sodium hydroxide to  $200^\circ$  it gives sodium salicylate (p. 355). When heated with ammonia it gives urea (*Eckenroth*, Ber. 23, 694). Mixed alkyl-phenyl carbonates, such as phenyl-ethyl carbonate,  $COOEtPh$ , are formed by the action of chloroformic esters on the sodium salts of phenols, or of alcohols on chloroformic phenyl esters, obtained from phenol by the action of carbonyl chloride, and by heating phenyl carbonate with an alcohol in the presence of urea (*Morel*, Bull. [3], 21, 815; *Cazeneuve*, C.r. 127, 111). They lose carbon dioxide when heated, being converted into phenol-alkyl ethers (*Obermiller*, Ber. 42, 2237).

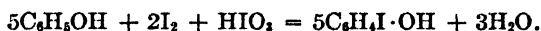
Diphenyl thiocarbonate,  $PhOCSOPh$ , m.p.  $106^\circ$ , and phenyl chloro-thiocarbonate,  $ClCSOPh$ , a yellow oil, b.p.  $91^\circ$  (10 mm.), are both obtained, under different conditions, by the action of thiophosgene on sodium phenate (*Eckenroth*, Ber. 27, 3410; *Rivier*, Bull. [3] 35, 837). Phenyl carbamate, phenylurethane,  $NH_2COOPh$ , m.p.  $141^\circ$ , can be obtained by adding mercury fulminate in small portions at a time to hot phenol (*Scholl*, Ber. 33, 51; *Gattermann*, Ann. 244, 43). Phenyl phenyl-carbamate,  $PhNHCOOPh$ , m.p.  $124^\circ$ , is obtained from carbanil (p. 97) and phenol (*Leuckart*, Ber. 18, 875; *Eckenroth*, Ber. 27, 1370). Phenyl diphenyl-carbamate,  $Ph_2NCOPh$ , m.p.  $105^\circ$ , is obtained from diphenyl-urea chloride and phenol (*Herzog*, Ber. 40, 1833). Phenyl phenyl-thiocarbamate,  $PhO-CSNHPh$ , unstable, colourless needles, is obtained from phenyl chlorothiocarbonate and aniline. Phenyl phenylimido-carbonate,  $PhN:C(OPh)_2$ , m.p.  $136^\circ$ , is obtained by the action of isocyanophenyl chloride (p. 95) on sodium phenate (*Scholl*, Ber. 28, 972). Phenyl allophanate,  $NH_2CONHCOOPh$ , a crystalline compound, is obtained by passing the vapour of cyanic acid into phenol.

**PHENYL ESTERS OF MONOBASIC CARBOXYLIC ACIDS**. When phenyl esters of organic acids are heated with aluminium chloride they undergo the Fries rearrangement into *o*- and *p*-acyl phenols (*Rosenmund*, Ann. 460, 56). The esters of aliphatic and araliphatic acids undergo this change more readily than those of aromatic acids. The opposite rearrangement, the migration of an acyl group into the OH group has also been observed with certain phenol-ketones. Phenyl formate, see *Seifert*, J. pr. 31, 467. Phenyl ortho-formate,  $CH(OPh)_2$ , m.p.  $76^\circ$ , b.p.  $265^\circ$  (50 mm.), is obtained by the action of chloroform on potassium phenate (*Auwers*, Ber. 18, 2656). Phenyl acetate,  $CH_3COOPh$ , b.p.  $195^\circ$  (*Kreysler*, Ber. 18, 1716), is decomposed when heated strongly with sodium into acetone, dehydracetic acid (2-methyl-benzo- $\gamma$ -pyrone), and a compound of the formula  $C_{11}H_8O_4$ , m.p.  $108-109^\circ$ , supposed to be  $\alpha$ -acetyl- $\beta$ -hydroxy-coumarin (p. 491) (*Perkin*, J. 119, 1284). For the formation of this compound from phenol and ketene, see *Rice*, Am. 56, 1764. Phenyl ortho-acetate,  $CH_3C(OPh)_2$ , m.p.  $98^\circ$  (*Heiber*, Ber. 24, 3678).

**PHENYL ESTERS OF DIBASIC CARBOXYLIC ACIDS.** Diphenyl oxalate,  $(\text{COOPh})_2$ , m.p.  $136^\circ$ , b.p.  $191^\circ$  (15 mm.) (*Bischoff*, Ber. 35, 3437). Ethyl phenyl oxalate,  $(\text{C}_2\text{H}_5)_2\text{C}_2\text{O}_4\text{Ph}$ , b.p.  $236^\circ$ , is obtained from ethyl oxalyl chloride (Vol. I, p. 538). Diphenyl malonate, m.p.  $50^\circ$  (*Bischoff*, Ber. 35, 3455). Diphenyl succinate, m.p.  $118^\circ$ , b.p.  $330^\circ$ . Diphenyl fumarate, m.p.  $161^\circ$ , decomposes on slow distillation in an atmosphere of carbon dioxide into phenyl cinnamate (p. 464) and stilbene (p. 559) (*Anschütz*, Ber. 18, 1948).

### *Substitution Products of Phenol*

**HALOGENO-PHENOLS.** *Methods of formation.*—(1) Chlorine and bromine act very readily on phenols; thus, bromine precipitates 2,4,6-tribromophenol quantitatively from an aqueous solution of phenol. Both chlorine and bromine enter the ortho- and para-positions. First 1,2- and 1,4-mono-, then 1,2,4-di-, and finally 1,2,4,6-tri-substitution products are formed. At  $150$ – $180^\circ$ , chlorine and gaseous bromine give good yields of *o*-chloro- and *o*-bromo-phenols (Ger. Pat. 76,597). Sulphuryl chloride acts upon phenol to give *p*-chlorophenol; it readily chlorinates the free phenols, but not their ethers. Iodo-substitution products are obtained by adding iodine and iodic acid to a solution of phenol in dilute potassium hydroxide (*Kekulé*, Ann. 137, 161):



They may also be obtained by the action of iodine and mercuric oxide on phenol, the chief product being 2,4-diiodophenol.

(2) In the phenol sulphonic and phenol-carboxylic acids, the sulphonic and carboxyl groups in the *o*- and *p*-positions to the phenol hydroxyl group are replaced by the action of chlorine or bromine (*Oberniller*, Ber. 42, 4361). (3) Halogen-substituted anilines may be converted into the corresponding phenols by diazotisation and boiling. This reaction gives pure mono-halogeno-phenols. (4) The  $\text{NO}_2$  group of nitrophenols may be replaced by halogen by reducing first to amine and then diazotising. (5) Halogen substituted phenol-carboxylic acids may be distilled with lime or baryta.

The energetic bromination of phenols may result not only in the substitution of nuclear hydrogen atoms, but even in the elimination of other groups, *e.g.*, nitro- and acetamino-groups, from the nucleus, and their replacement by bromine. Bromine may also substitute in the acetamino-group (*Heller*, J. pr. 129, 214).

*Reactions.*—1. The acidic character of phenol is greatly accentuated by the introduction of halogen atoms into the benzene nucleus. Thus, trichlorophenol readily decomposes alkali carbonates. 2. When fused with caustic potash the halogens are replaced by hydroxyl groups (p. 185). In this reaction, especially if the temperature is high, the hydroxyl group does not always enter in the same position as the halogen replaced, but there is often a rearrangement into more stable isomers. Thus, all three chlorophenols give resorcinol. It is not possible, therefore, to use this reaction as a method of determining constitution.

3. The halogens are replaced by hydrogen by the action of sodium amalgam, or by heating an aqueous alkaline solution of the chloro-, bromo-, or iodo-phenol with iron filings under pressure (Ger. Pat. 396,454). 4. The bromine atoms in ortho- and para-positions to hydroxyl in bromophenols are readily replaced by  $\text{NO}_2$  by the action of nitrous acid (*Dahmer*, Ann. 333, 346; *Zincke*, J. pr. 61, 561).

**MONOHALOGENO-PHENOLS.** The monochloro-phenols, in particular.

are characterised by an unpleasant, persistent odour. Some are powerful disinfectants, *e.g.*, *p*-chloro-*m*-cresol and *p*-chloro-*sym*-xylenol (*Jentic*, C. 1932, I, 1556). When fused with potash the bromo- and iodo-phenols are attacked at a lower temperature than the chloro-compounds, and give the corresponding dihydroxy-benzenes. The *o*- and *p*-compounds give a larger yield of resorcinol the higher the temperature of the fusion, and the three monochloro-phenols give resorcinol only.

| Phenol        | ortho- |      | meta- |      | para- |      |
|---------------|--------|------|-------|------|-------|------|
|               | M.p.   | B.p. | M.p.  | B.p. | M.p.  | B.p. |
| Chloro-phenol | 90°    | 176° | 33°   | 214° | 43°   | 217° |
| Bromo-phenol  | Liquid | 195° | 32°   | 236° | 63°   | 238° |
| Iodo-phenol   | 43°    | ..   | 40°   | ..   | 94°   | ..   |

**IODOANISOLE**s and **-PHENETOLE**s, see *Reverdin*, Ber. 29, 997, 1409, 2595.

**POLYHALOGENO-PHENOLS**. Direct substitution leads to the preferential formation of 2,4-di- and 2,4,6-trihalogeno-phenols. A tetrachloro-phenol is ultimately obtained on prolonged chlorination (*Barral*, Bull. [3] 27, 1874). For the iodination of phenol see *Brenans*, C.r. 132, 831; 134, 357; *Richard*, Pharm. chim. 1902.

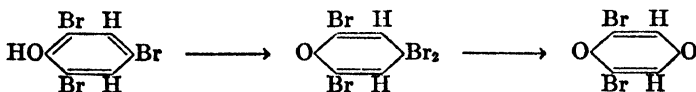
| Phenol                                  | M.p. | B.p. | Phenol                              | M.p. | B.p. |
|-----------------------------------------|------|------|-------------------------------------|------|------|
| 2,4-Dichloro-phenol                     | 45°  | 210° | 2,4,5-Trichloro-phenol <sup>c</sup> | 63°  | ..   |
| 2,5-Dichloro-phenol                     | 58°  | 211° | 2,4,6-Trichloro-phenol              | 70°  | 246° |
| 2,4-Dibromo-phenol                      | 40°  | 239° | 2,4,6-Tribromo-phenol               | 93°  | ..   |
| 2,4-Diiodo-phenol                       | 72°  | ..   | 2,3,5-Tribromo-phenol <sup>d</sup>  | 92°  | ..   |
| 2,5-Dichloro-3,4,6-tribromo-phenol      | 206° | ..   | 2,4,6-Triiodo-phenol                | 158° | ..   |
| 2,3,4,6-Tetrachloro-phenol <sup>a</sup> | 70°  | ..   | 3,5,6-Triiodo-phenol <sup>a</sup>   | 114° | ..   |
| 2,3,4,6-Tetrabromo-phenol <sup>b</sup>  | 120° | ..   | Pentachloro-phenol                  | 189° | ..   |
|                                         |      |      | Pentabromo-phenol                   | 225° | ..   |

<sup>a</sup> *Biltz*, Ber. 37, 4013. <sup>b</sup> *Körner*, Ann. 137, 209. <sup>c</sup> *Kohn*, Mo. 58, 73. <sup>d</sup> *Bamberger*, Ber. 39, 4251. <sup>e</sup> *Brenans*, C.r. 137, 1065.

For the six isomeric dichloro-phenols, see *Hollemann*, Rec. 37, 96, and for the isomeric trichloro-phenols, see *Tiessens*, Rec. 50, 112.

The silver salts of tribromo- and some other polybromo-phenols exist in two forms, an unstable, orange-red form, and a stable, white form. This allotropism is still unexplained (*Hantzsch*, Ber. 40, 4875).

The tri-, tetra-, and penta-chloro- and -bromo-phenols add on chlorine and bromine, with formation of chloro- and bromo-*oxy-di*- and -*oxy-tetrahydrobenzenes*. The halogeno-phenols can be obtained from these by reduction (*Biltz*, Ber. 37, 4010). Tribromo-phenol combines with a further quantity of bromine giving **tribromo-phenol bromide**, C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>OBr, m.p. 148° (*Auwers*, Ann. 202, 133; *Lewis*, J. 131, 1001; *Sauknevitich*, J. pr. 138, 20). This is easily reconverted into tribromo-phenol, but rearranges to tetrabromo-phenol, C<sub>6</sub>Br<sub>4</sub>H(OH) on treatment with conc. sulphuric acid and gives dibromo-quinone (p. 238) on digestion with lead acetate. Hence it should be regarded as *p*-**keto-dihydro-tetrabromobenzene**:

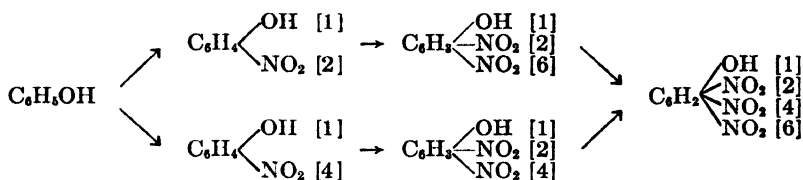


(*Thiele*, Ber. 33, 673; *Castle*, Am. Chem. J. 27, 31). Trichloro-phenol is oxidised to dichloro-quinone by nitric acid (*Leger*, C.r., 146, 694).

*The Nitrophenols*

The phenols are nitrated with the same ease as the anilines. The acidic character of the phenols is considerably enhanced by the introduction of nitro-groups. The nitrophenols themselves decompose the alkali carbonates. Trinitrophenol is a true acid. Its chloride,  $C_6H_2(NO_2)_3Cl$ , is decomposed by water with re-formation of trinitrophenol (p. 63). Halogens are readily introduced into the benzene nucleus of nitrophenols, whereas the nitro-hydrocarbons are rather difficult to chlorinate.

The nitro-groups replace the *o*- and *p*-hydrogen atoms relative to hydroxyl, and enter *m*-positions to each other, according to the scheme:



The free nitrophenols, which are either colourless or slightly yellow, are undoubtedly true phenols, but their salts which are intensely coloured in shades ranging from yellow to red are very probably de-

rived from a hypothetical nitronic acid,  $O=C_6H_4=N-OH$ , the *aci*-nitrophenol form (Hantzsch, Ber. 39, 1084), like the coloured salts of the nitroparaffins.

Strong evidence for this view is given by Hantzsch's observation (Ber. 39, 1073) that the nitrophenol ethers exist in two isomeric forms. Although the normal ethers are colourless, small quantities of intensely red, very unstable ethers are obtained by the action of alkyl halides on the silver salts of nitroparaffins. They isomerise spontaneously to the colourless ethers, and are rapidly hydrolysed by water, the nitrophenols being regenerated. These unstable ethers correspond to the highly coloured salts of the nitrophenols, and their structure is most probably quinoid:  $O=C_6H_4=NOOCH_3$ . Only the colourless normal ethers of *m*-nitrophenols have so far been obtained, which agrees with the fact that *m*-quinones do not exist.

Attempts to isolate the *aci*-forms of free nitrophenols have hitherto failed. However, although some of them (such as *p*-nitrophenol, 2,4-dinitrophenol, etc.) are colourless in the solid state, others (such as *o*-nitrophenol) are yellow, and Hantzsch believes that the latter are to be regarded as solid solutions of a certain amount of an *aci*-form in a large excess of the true colourless nitrophenol.

**MONONITROPHENOLS,  $NO_2.C_6H_4.OH$ .** When dilute nitric acid acts upon phenol, *o*- and *p*-mononitrophenols are formed. In the cold, the *p*-compound is the chief product; at  $-67^\circ$  under the influence of electrical sparks, the yield of the *p*-compound is five times that at  $-40^\circ$  (Pictet, C.r. 116, 815). The *o*- and *p*-compounds are separated by steam distillation, the *p*-compound not being vola-



tile, or by means of acetylene dichloride (*Mann*, Ch. Ztg., 56, 542). In the presence of sulphuric acid, phenol is nitrated by nitrogen dioxide (*Armstrong*, Proc. 1891, 91). The first product in the nitration of phenol is a nitroso-compound; nitric acid dissociates into  $O + HNO_2$ , and it is the latter which effects the nitrosation. More nitric acid converts the  $NO$  into a  $NO_2$  group, with formation of  $HNO_2$  (*Kartaschew*, J. Russ. Phys. Chem. Soc. 62, 2129).

*o*-Nitrophenol, together with a little of the *p*-compound, is also obtained by heating nitrobenzene with dry caustic potash (p. 59), and from the reaction product of nitrobenzene and sodium by passing air through it. *o*- and *p*-Nitrophenols are obtained from the corresponding chloro- and bromo-nitrobenzenes by the action of caustic potash at  $120^\circ$ . Under these conditions, *m*-bromonitrobenzene does not react. Similarly, *o*- and *p*-nitrophenol are obtained from the corresponding nitranilines by heating with alkalis. *m*-Nitrophenol is prepared from ordinary dinitrobenzene, which is reduced to *m*-nitraniline. This is converted into the diazonium sulphate, and finally by boiling with dilute sulphuric acid into *m*-nitrophenol. For its preparation, see *Meldola*, J. 103, 876. *p*-Nitrophenol has been made from aliphatic compounds by acting on nitromalonic aldehyde with acetone (p. 25). It is obtained by oxidation of *p*-nitrosophenol with nitric acid (*Robertson*, J. 81, 1475). When benzene is nitrated in the presence of mercuric nitrate, *o*-nitrophenol is formed together with some polynitrophenols (Ger. Pats. 194,883 and 214,045).

|                                                                 | Methyl ether                             | Ethyl ether      |
|-----------------------------------------------------------------|------------------------------------------|------------------|
| <i>o</i> -Nitrophenol, m.p. $45^\circ$ , b.p. $214^\circ$ ..... | m.p. $+10^\circ$ , b.p. $273^\circ$ .... | b.p. $267^\circ$ |
| <i>m</i> -Nitrophenol, m.p. $96^\circ$ .....                    | m.p. $38^\circ$ , b.p. $258^\circ$ ..... | m.p. $34^\circ$  |
| <i>p</i> -Nitrophenol, m.p. $114^\circ$ (two forms)....         | m.p. $55^\circ$ , b.p. $260^\circ$ ..... | m.p. $60^\circ$  |

*o*- and *m*-Nitrophenols form yellow crystals. The *m*-compound is fairly soluble in water. The *o*-compound has a sweetish taste. Its sodium salt forms dark-red prisms. The almost colourless  $\alpha$ -form of *p*-nitrophenol crystallises from toluene above  $63^\circ$ , and the yellowish  $\beta$ -form below this temperature. Both form prismatic crystals (C. 1916, I, 299). *p*-Nitrophenol crystallises from hot water in colourless needles, and its potassium salt in golden-yellow needles with  $2H_2O$ . With mercuric oxide or acetate the nitrophenols first give true mercury phenates,  $(NO_2 \cdot C_6H_4O)_2Hg$ , which change to mercuri-nitrophenols, with migration of Hg into the nucleus. These latter readily form highly coloured mercuri-anhydrides,

presumably derived from the structure  $O : C_6H_3 \begin{matrix} \diagup NO \\ \diagdown Hg \end{matrix} O$  (*Hantzsch*, Ber. 39,

1105). On bromination, *p*-nitrophenol gives 2,6-dibromo-4-nitrophenol, m.p.  $141^\circ$ . 4,6-Dibromo-2-nitrophenol, m.p.  $117^\circ$ , is obtained by the action of ethyl nitrite on an alcoholic solution of 2,4,6-tribromophenol. See p. 197 for the displacement of Br by  $NO_2$  in bromophenols. *o*-Nitrophenyl-ether,  $PhO \cdot C_6H_4 \cdot NO_2$ , b.p.  $233^\circ$  (60 mm.). *p*-Nitrophenyl-ether, m.p.  $65^\circ$  (C. 1916, II, 2009). *o,o'*-Dinitrophenyl ether,  $(NO_2 \cdot C_6H_4)_2O$ , m.p.  $114^\circ$  (*Ullmann*, Ber. 29, 1880; *Häusermann*, Ber. 29, 2084; *Cook*, Am. 25, 60).

**DINITROPHENOLS**,  $(NO_2)_2C_6H_4OH$ .  $\alpha$ - or 2,4-Dinitrophenol, m.p.  $114^\circ$ , and  $\beta$ -, or 2,6-dinitrophenol, m.p.  $64^\circ$ , are both produced in the nitration of phenol (*Marqueyrol*, Bull. 25, 370, 375), or of *o*-nitrophenol, and the  $\alpha$ -compound in the nitration of *p*-nitrophenol. They can also be obtained by the action of alkaline potassium ferricyanide on *m*-dinitrobenzene. The  $\alpha$ -methyl ether, m.p.  $86^\circ$ , is converted into 2,4-dinitraniline by heating with ammonia (cf. picric acid). Three isomeric dinitrophenols of m.p.  $104^\circ$ ,  $134^\circ$ , and  $141^\circ$  are produced by the nitration of *m*-nitrophenol (*Holleman*, Rec. 21, 432; *Steinmetz*, C. 1915, I, 884). On further nitration these give trinitrophenols and trinitroresorcinol (p. 223). *sym*-Dinitro-phenetole,  $C_2H_5O[1]C_6H_3[3,5](NO_2)_2$ , m.p.  $96^\circ$  is obtained by the action of sodium ethylate on trinitrobenzene (*Vermeulen*, Rec. 25, 12).

**TRINITROPHENOLS**. Picric acid,  $(NO_2)_3C_6H_2OH$ , m.p.  $122^\circ$ , is produced by the nitration of phenol, of 1,2- and 1,4-nitrophenols,

and of the two dinitrophenols. It is also obtained by the oxidation of *sym*-trinitrobenzene with potassium ferricyanide. This indicates that it is 2,4,6-trinitrophenol. It can be obtained from benzene in one operation by the action of nitric acid in the presence of mercuric nitrate (*Vignon*, Bull. 27, 547). It is produced when a large number of organic substances, such as indigo, aniline, resins, silk, leather, wool, etc., are treated with nitric acid.

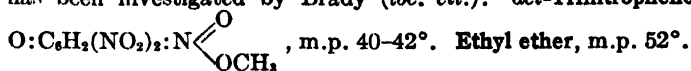
*History*.—*Woulfe* (1711) found that when indigo is treated with nitric acid a liquid is obtained which colours silk yellow. In 1799, *Welter* prepared pure picric acid by nitrating silk, and it was accordingly called "Welter's bitter." *Liebig* called it carbon-nitrogen acid or carbazotic acid. *Dumas* analysed the acid and called it picric acid from the Greek *pikros*, bitter. *Laurent* (1848) recognised it as a derivative of phenol.

*Properties*.—Picric acid crystallised from hot water or alcohol in yellow leaflets or prisms, and has a very bitter taste. It dissolves in 160 parts of cold water, and fairly freely in hot water. It dyes silk and wool a beautiful yellow tinged with green from an acid bath. On heating it sublimes without decomposition.

*Reactions*.—Picric acid combines with many benzene hydrocarbons, such as benzene, naphthalene, anthracene, and with many other aromatic compounds, forming molecular compounds, which crystallise very well, and can be used for characterising and separating aromatic hydrocarbons of high molecular weight (*Jefremov*, J. Russ. Phys. Chem. Soc. 50, 372). Chlorine or phosphorus pentachloride convert picric acid into picryl chloride (p. 63). When a solution of barium picrate is boiled with barium hydroxide, hydrogen cyanide is formed. When a hot aqueous suspension of bleaching powder acts upon picric acid, chloropicrin,  $\text{CCl}_3(\text{NO}_2)$  (Vol. I, p. 485) is formed. By the action of potassium cyanide on picric acid, potassium isopurpurate,  $\text{C}_6\text{H}_2\text{N}_3\text{O}_6\text{K}$ , is formed in brown leaflets with a greenish-golden lustre. This was formerly on the market under the name of *grenat soluble*. Isopurpuric acid can be obtained from its potassium salt by the addition of phosphoric acid. It is dark-violet in colour, and according to its reaction products its structure must be  $\text{C}_6[2,6](\text{CN})_2[1,3](\text{NO}_2)_2[4,5](\text{OH})(\text{NHOH})$ . *o,p*- and *o,o*-Dinitrophenols and other polynitrophenol derivatives react similarly with potassium cyanide (*Borsche*, Ber. 37, 1843, 4388; 38, 3538, 3938).

*Salts and ethers*.—The potassium salt,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OK}$ , crystallises in yellow needles which dissolve in 260 parts of water at  $15^\circ$ . The sodium salt dissolves in 10 parts of water at  $15^\circ$ , and is separated from its solution by the addition of sodium carbonate solution. The ammonium salt forms beautiful large needles, and is used in explosive mixtures. All the picrates explode with great violence when heated or struck.

*Methyl ether*, 2,4,6-trinitroanisole, m.p.  $65^\circ$ , obtained by nitrating anisole, combines readily with tertiary alkylamines, forming picrates of N-alkylated quaternary bases (*Kohn*, Mo. 34, 1751). *Ethyl ether*, m.p.  $78^\circ$ , is obtained from picric acid and orthoformic ester (*Walther*, J. pr. 91, 258). Additive salts are formed from these ethers and sodium alkylates, in the same manner as from trinitrobenzene (p. 61) (*Brady*, J. 127, 2230). The alcoholysis of the two ethers has been investigated by *Brady* (*loc. cit.*). *aci*-Trinitrophenol-methyl ether,



2,3,6-Trinitrophenol, m.p.  $117^\circ$ . 2,4,5-Trinitrophenol, m.p.  $96^\circ$ . These two compounds are among the products obtained by further nitration of dinitrophenols derived from *m*-nitrophenol. 2,3,4-Trinitroanisole, m.p.  $155^\circ$  is obtained from 2,3-dinitroanisole (*Vermeulen*, Rec. 31, 101). 2,3,5-Trinitroanisole, m.p.  $104^\circ$ . 3,4,5-Trinitroanisole, m.p.  $119\text{--}120^\circ$ . 3,4,6-Trinitroanisole, m.p.  $106\text{--}107^\circ$  (*Vermeulen*, Ak. Amst. 20, 807).

**Tetranitrophenol**, m.p. 130°, forms golden yellow needles, and is highly explosive. It is obtained by oxidising diquinoyl-trioxime (p. 242). The position of the nitro-groups is unknown (*Nielski*, Ber. 30, 184). 2,3,5,6-Tetranitroanisole, exists in two forms, m.p. 112° and 154° (*Blanksma*, Rec. 23, 111, 119).

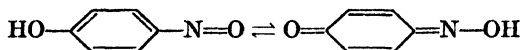
**NITROCRESOLS.** *o*-Nitro-*p*-cresol,  $\text{NO}_2[\text{2}]\text{CH}_3[\text{4}]\text{C}_6\text{H}_4\text{OH}$ , m.p. 79°, and *p*-nitro-*o*-cresol, m.p. 118°, are prepared in a pure state from the corresponding nitrotoluidines. The former is also easily obtained by nitrating *p*-cresol carbonate and hydrolysing the product. *m*-Nitro-*p*-cresol, m.p. 32°, which is simultaneously formed, is volatile with steam, and can thus be separated (Ger. Pat. 206,638; *Holleman*, Rec. 36, 271). It is decomposed by the action of fuming sulphuric acid, isoprene-lactonic acid being formed (p. 29) (*Pauly*, Ann. 416, 1). By further nitration of the methyl ethers of *o*-nitro-*p*-cresol, and *p*-nitro-*o*-cresol, *o*-dinitro-compounds are obtained (*Kauffer*, Ber. 34, 2238). Dinitro-derivatives are readily obtained by nitration of *o*- and *p*-cresols. One of these, 2,6-dinitro-*p*-cresol, m.p. 84°, is used in the form of its sodium salt as an orange-yellow dye, known as *victoria orange* or *saffron substitute*. Dinitro-*o*-cresol, in the form of solutions of its salts, is used as an insecticide, under the name of *antinonin*, especially for combating *Ocenaria monacha* (Ber. 27, II 316). 2,6-Dinitro-4-*tert*-butyl-*m*-cresol methyl ether, m.p. 85°, obtained by nitrating 4-*tert*-butyl-*m*-cresol methyl ether, m.p. 23.4°, or aceto-*iso*-butyl-*m*-cresol methyl ether, m.p. 91°, is used in perfumery as a synthetic musk (*ambretto musk*) (*Darzens*, C.r. 193, 321; *Seide*, C. 1933, I, 603). When *m*-cresol is nitrated a trinitrocresol,  $(\text{NO}_2)_3\text{C}_6\text{H}(\text{CH}_3)\text{OH}$ , m.p. 106°, is formed. It is also obtained from nitrococcic acid (p. 363), and by nitrating thymol (p. 190) (C. 1901, II, 411). Tetranitro-*m*-resorcinol, m.p. 175° (C. 1908, I, 724). Nitroxylenols, see *Diepolder*, Ber. 42, 2917.

Nitration of *p*-*tert*-butyl-phenol, m.p. 97° produces 2,6-dinitro-4-*tert*-butyl-phenol, m.p. 96°, and this, when vigorously nitrated, loses a methyl group and becomes tetranitro-*p*-*iso*-propyl-phenol, m.p. 122–123° (*Schaaf*, J. pr. 133, 173).

**HALOGENO-NITROPHENOLS.** Numerous halogeno-nitrophenols have been prepared by the action of halogens on nitrophenols, or by nitrating halogenophenols (*Meldola*, J. 73, 681). *p*-Nitro-*o*-iodoanisole,  $\text{C}_6\text{H}_3[\text{4}]\text{NO}_2[\text{2}]\text{I}[\text{1}]\text{OCH}_3$ , is formed, rather unexpectedly, by the nitration not only of *o*- but also of *p*-iodo-anisole. In the latter case the iodine atom migrates (*Reverdin*, Ber. 29, 997; *Robertson*, J. 101, 1964). This migration of the halogen in the nitration of *p*-halogeno-phenols has been further studied by *Gibbs* and *Robertson*, J. 105, 1885.

### Nitrosophenols

The *p*-nitrosophenols are desmotropic with the quinone-monoximes



*i.e.*, the two molecules are so readily converted into each other by a migration of a H atom (prototropism) and a simultaneous change in the system of linkages, that the formation of the oxime of the quinone and the introduction of a nitroso-group into the phenol, or the introduction of a hydroxyl group into the nitroso-compound, results in the same product (*Goldschmidt*, Ber. 17, 801). General experience with desmotropic substances (Vol. I, p. 48) indicates the existence of an equilibrium between the two kinds of molecules in the liquid or dissolved state. In the solid state quinone-oxime and nitrosophenol may exist as separate individuals, and the one or the other may be produced regardless of the method of preparation. In the anion of their alkali salts the system of linkages is probably not fixed in the way indicated by either of the above formulae. For *o*-nitrosophenols a corresponding desmotropism with *o*-quinone-monoximes is to be assumed.

Nitrosophenols are formed: 1. By the action of nitrous acid on phenols (*Baeyer*, Ber. 7, 964; cf. *Hodgson*, J. 1932, 866) when the monohydric phenols form mononitroso-compounds, and *m*-dihydroxybenzenes, such as resorcinol, form dinitroso-compounds.

The method may be used as follows: (a) Nitrous acid, produced by the action of dilute sulphuric or acetic acid on alkali nitrites, is allowed to act on phenols (*Baeyer*, Ber. 7, 967; 8, 614). (b) The nitrites of heavy metals are decomposed by phenols themselves (*Köhler*, Ber. 16, 3080). (c) Nitrosyl-sulphuric acid,  $\text{NO} \cdot \text{OSO}_3\text{H}$ , or nitrosyl chloride,  $\text{NOCl}$ , are allowed to act on phenols (*Stenhouse*, Ann. 188, 353; *Nietzki*, Ber. 21, 429). (d) Amyl nitrite and sodium phenates are allowed to interact (*Goldschmidt*, Ber. 17, 803).

2. By boiling *p*-nitroso-alkylanilines, such as *p*-nitroso-dimethylaniline (p. 105) with alkalis:



3. By reducing an acetic acid solution of *o*-nitrophenol with zinc dust, when *o*-nitrosophenol is formed (*Baudisch*, Ber. 51, 1058).

4. By oxidising aminophenol ethers with permonosulphuric acid, or hydroxylaminophenol ethers with ferric chloride or silver oxide, and hydrolysing the resulting ethers.

5. By acting on aqueous or alcoholic solutions of quinones with hydroxylamine hydrochloride (free hydroxylamine reduces quinones to hydroquinones) (*Goldschmidt*, Ber. 17, 2061).

***o*-Nitrosophenol**,  $\text{HO} \cdot \text{C}_6\text{H}_4[2]\text{NO}$ . *o*-Anisidine is oxidised by Caro's acid to *o*-nitrosoanisole,  $\text{CH}_3\text{OC}_6\text{H}_4[2]\text{NO}$ , m.p.  $103^\circ$ , which is hydrolysed by potassium bisulphate to *o*-nitrosophenol (*Baeyer*, Ber. 35, 3036). The reaction is analogous to the oxidation of aniline to nitrosobenzene. For the preparation of *o*-nitrosophenol from *o*-nitrophenol, see above. Another method consists of reducing *o*-nitrophenol *p*-toluene sulphonate to a hydroxylamine, oxidising this with silver oxide and hydrolysing the nitroso-ester (*Baudisch*, Ber. 48, 1660). For preparation from *o*-anisyl hydroxylamine see *Müller*, Ann. 495, 143. *o*-Nitrosophenol forms greenish yellow needles, and is exceedingly volatile. Its solution in ligroin is green, and its potassium salt forms dark-red leaflets. With heavy metals it forms intensely coloured complex salts, and can be used for detecting minute traces of copper (*Baudisch*, Ber. 48, 1660; 51, 1058). ***m*-Nitrosoanisole**, m.p.  $48^\circ$ , is obtained from *m*-nitroanisole (*Baudisch*, Ber. 48, 1665).

***p*-Nitrosophenol, quinone monoxime**, is also produced from nitrosobenzene by the action of caustic soda (*Bamberger*, Ber. 33, 1954). It crystallises from hot water in slender, colourless needles, which readily turn brown, and from ether in large brownish-green flakes. It dissolves in water, alcohol, or ether with a bright green colour. It melts with decomposition on heating. Its sodium salt crystallises in red needles with  $2\text{H}_2\text{O}$ .

In their conversion into quinone-dioxime, the formation of nitrosophenol hypochlorites,  $\text{C}_6\text{H}_4(\text{O})\text{NOCl}$ , by the action of hypochlorous acid, and in their feebly basic character, the nitrosophenols have the characteristics of quinone-oximes (*Liebermann*, Ber. 18, 3198; *Möhlau*, Ber. 19, 280). When *p*-nitrosophenol is methylated quinone-methoxime,  $\text{O} : \text{C}_6\text{H}_4 : \text{NOCH}_3$ , m.p.  $83^\circ$ , is formed, and not nitrosoanisole. ***p*-Nitrosoanisole**,  $\text{CH}_3\text{OC}_6\text{H}_4[4]\text{NO}$ , m.p.  $23^\circ$ , is obtained by oxidation of *p*-anisidine with permonosulphuric acid (Caro's acid) or by the action of ferric chloride on *p*-anisole-hydroxylamine (*Rising*, Ber. 37, 44). It is easily hydrolysed by dilute sulphuric acid to *p*-nitrosophenol (*Baeyer*, Ber. 35, 3034).

It is not yet possible to say which crystalline form of *p*-nitrosophenol has the nitrosophenol formula and which the quinone oxime, though the green colour of the crystals deposited from ether solution seems to indicate that these are the true nitrosophenol. *Anderson* and *Geiger* (Am. 54, 3064) by comparing the absorption curves of the ether solution with those of the two methyl ethers, conclude that the substance is present to the extent of 70% as quinone monoxime at equilibrium. *Hodgson* (J. 1931, 1494) has shown that when an ether solution of diazomethane acts on *p*-nitrosophenol, the glyoxime dinitron of *p*-nitrosoanisole is the chief product. This is clearly derived from the nitrosophenol molecule. At the same time a smaller quantity of quinone-monoxime O-methyl ether is formed. It follows that both forms must be present in the original substance, but that the nitrosophenol predominates.

The nitrosophenols can be converted into nitrosoanilines. By the action of hydrochloric acid nitrosophenol is converted into dichloroaminophenol, and this with nitrous acid and hydroxylamine gives "*p*-diazophenol":



In a similar way it forms azo-compounds (p. 208) with amines. It is readily reduced by phenylhydrazine to aminophenol (*Plancher*, Gazz. 25, II, 379). For the action of diazonium compounds see *Borsche*, Ber. 32, 2935; *Ann.* 312, 211. On adding a little concentrated sulphuric acid to a mixture of nitrosophenol and phenol, a deep-red colour is produced, turning deep blue on addition of alkali (*Liebermann's* reaction, p. 186). For halogenated nitrosophenols, see *Hodgson*, J. 1931, 1494.

**Nitroso-*o*-cresol**, m.p. 134°, is obtained from *o*-cresol (p. 189) or from toluquinone (p. 238). For a bluish-violet dye obtained from *p*-nitroso-*o*-cresol, see *Bovini*, C. 1928, I, 1025. **Nitroso-*m*-cresol**, m.p. 155° (*Mehue*, Ber. 21, 729; *Cecelsky*, Mo. 20, 779). **Nitrosothymol**, m.p. 163° (*Goldschmidt*, Ber. 17, 2061; *Kehrmann*, Ann. 310, 89).

### Aminophenols

The aminophenols are obtained by the reduction of nitro- or nitrosophenols, or hydroxyazo-compounds (p. 209; *Oddo*, Ber. 38, 2751). Ammonium sulphide reduces some of the nitro-groups of polynitrophenols, while tin and hydrochloric acid reduces them all (p. 72). For special methods of formation see *m*- and *p*-aminophenol.

**Reactions.**—The free aminophenols decompose readily, especially when exposed to moist air or light. The acidic nature of the phenols is much less marked when the amino-group is present (*cf.* however, *Raikov*, Chem. Ztg. 27, 781). The three aminophenols form coloured double compounds with the zinc halides ( $\text{C}_6\text{H}_7\text{ON}$ )<sub>2</sub>ZnHal<sub>2</sub> (*Koppitz*, J. pr. 88, 744). They give aminophenoxyacetic acids with chloroacetic acid (*Jacobs*, Am. 39, 2188).

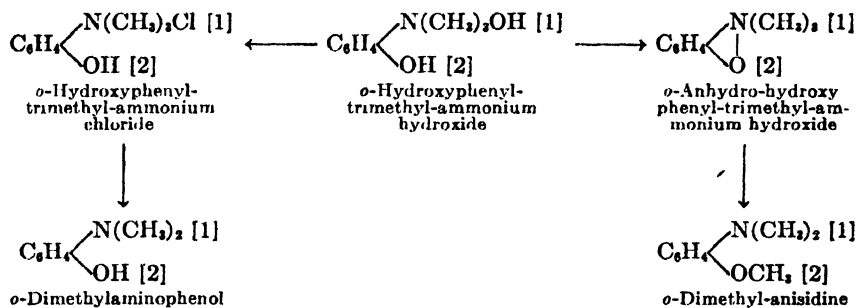
Like the *o*-phenylene-diamines, the *o*-aminophenols readily form heterocyclic compounds, *anhydrobases*, *benzoxazoles*, which correspond to the benzimidazoles. Similar compounds, benzothiazoles are derived from the *o*-aminothiophenols. Amino- and acetaminophenol ethers, see *Heidelberger*, Am. 41, 1450.

***o*-Aminophenol**,  $\text{NH}_2[2]\text{C}_6\text{H}_4[1]\text{OH}$ , m.p. 170°, has been prepared by *Brown* and *Carrick* (Am. 41, 436) by hydrogenating *o*-nitrophenol catalytically at 265° in the presence of copper or nickel. It is only slightly soluble in water. ***o*-Anisidine**,  $\text{NH}_2[2]\text{C}_6\text{H}_4[1]\text{OCH}_3$ , b.p. 218°; acetyl-compound, m.p. 75°. **3-Amino-4-hydroxytoluene**,  $\text{NH}_2[3]\text{C}_6\text{H}_3[1]\text{CH}_3[4]\text{OH}$ , m.p. 133–134°, is obtained from *o*-nitro-*p*-cresol by electrochemical reduction in sodium carbonate solution (*Bradt*, J. Phys. Chem. 34, 2711).

***o*-Imino-diphenyl oxide, phenoxazine**,  $\text{O} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{NH}$ , is dealt with under the

diheteroatomic six-membered heterocyclic compounds; see also pyrocatechol, p. 218.

**Methylation of the amino-group in *o*-aminophenol.**—When a methyl alcoholic solution of *o*-aminophenol is treated with methyl iodide and caustic alkali, and after the methylation is complete, hydriodic acid is added, the iodide of an ammonium base is obtained. From this the ammonium hydroxide itself can be produced by treatment with moist silver oxide. The hydroxide loses water at 105°, and is converted into a cyclic ammonium compound resembling a betaine (Vol. I, p. 380), which is regarded as *o*-trimethyl-ammonium-phenol. It rearranges to *o*-dimethyl-anisidine when heated. The hydrochloride of the ammonium base decomposes into methyl chloride and *o*-dimethylaminophenol, m.p. 45°.



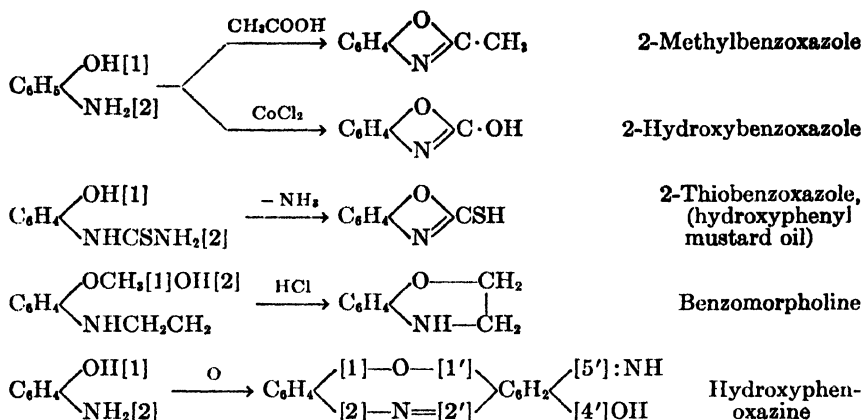
***o*-Methylaminophenol**,  $\text{CH}_3\text{NH}[2]\text{C}_6\text{H}_4[1]\text{OH}$ , is obtained from *o*-methylanisidine,  $\text{C}_6\text{H}_4(\text{NHCH}_3)\text{OCH}_3$ . Mixed with hydroquinone, its sulphate is used as a photographic developer under the name "Ortol" (Drevolder, Ber. 32, 3514); cf. also *Metol*. ***o*-Hydroxyethyl-anisidine**,  $\text{HO}\cdot\text{CH}_2\text{CH}_2\text{NH}[2]\text{C}_6\text{H}_4[1]\text{OCH}_3$ , b.p. 305°, is obtained from *o*-anisidine and ethylene chlorhydrin.

***o*-Formylaminophenol**,  $\text{CHO}\cdot\text{NHC}_6\text{H}_4\text{OH}$ , m.p. 129°, is obtained from *o*-aminophenol and formic acid, and also, together with *anthranil*, by the oxidation of *o*-aminobenzaldehyde with permonosulphuric acid, presumably owing to a rearrangement of *o*-hydroxylamino-benzaldehyde,  $\text{CHO}\cdot\text{C}_6\text{H}_4\text{NHOH}$ . At 160–170° it is converted into benzoxazole (Bamberger, Ber. 36, 2042). For acylated *o*-aminophenols, see Tingle, Am. 37, 51. When an aminophenol has two different acyl groups, one in the amino-group and the other in the hydroxyl, these acyl groups sometimes change places in alcoholic solution, the "heavier" group wandering from the amino-radical to the OH group. Thus, *o*-benzoylamino-phenyl acetate becomes *o*-acetamino-phenyl benzoate (Bell, J. 1931, 2962).

***o*-Hydroxyphenyl-urethane**,  $\text{C}_2\text{H}_5\text{COO}\cdot\text{NH}[2]\text{C}_6\text{H}_4[1]\text{OH}$ , m.p. 86°, is obtained by reduction of *o*-nitrophenyl-ethyl carbonate, through a rearrangement of the *o*-aminophenyl-ethyl carbonate,  $\text{NH}_2[2]\text{C}_6\text{H}_4[1]\text{O}\cdot\text{COOC}_2\text{H}_5$ , first formed. The hydrochloride has m.p. 151° (Ransom, Am. Ch. J. 23, 1; Stieglitz, Am. Ch. J. 31, 458; 32, 13). This change of an O-acyl to an isomeric N-acyl compound is quite a general reaction of *o*-aminophenols, and it takes place so readily that O-acyl-*o*-aminophenols can usually not be isolated. Cf. the similar changes of *o*-hydroxy-benzylamines and *o*-aminobenzoyl alcohols (Aauvers, Ann. 332, 159; 364, 147).

***o*-Hydroxyphenylurea**,  $\text{NH}_2\text{CONH}[2]\text{C}_6\text{H}_4[1]\text{OH}$ , m.p. 151°. ***o*-Hydroxyphenylthiourea**,  $\text{NH}_2\text{CSNH}[2]\text{C}_6\text{H}_4[1]\text{OH}$ , m.p. 161°. ***o*-Hydroxydiphenylamine**  $\text{OH}[2]\text{C}_6\text{H}_4[1]\text{NHC}_6\text{H}_5$ , m.p. 70°, is obtained by the action of acetyl or benzoyl peroxide on diphenylamine (Gamburjan, Ber. 42, 4003).

**CONDENSATIONS OF *o*-AMINOPHENOLS.** (1) *o*-Aminophenol gives benzoxazoles with carboxylic acids, e.g., 2-methylbenzoxazole with acetic acid. (2) With phosgene it gives 2-hydroxybenzoxazole or carbonyl-amino-phenol. The latter is also obtained by heating *o*-hydroxyphenyl-urea. (3) Hydroxyphenylthiourea gives 2-thiobenzoxazole, known as *o*-hydroxyphenyl mustard oil, on heating. (4) *o*-Hydroxyethyl-anisidine (see above) is converted into benzomorpholine when heated with HCl. (5) Oxidising agents convert *o*-aminophenol into hydroxy-phenoxazime. *o*-Aminophenol condenses with catechol to give phenoxazine. These products are dealt with in detail in Vol. IV.



*m*-Aminophenol, m.p. 122°, is obtained from *m*-nitrophenol (Bamblin, Ber. 11, 2101), from the oxaminic compound of *m*-phenylene diamine (Ger. Pat. 77, 131), by fusing metanilic acid with caustic soda (Meyer, Ber. 32, 2112), and by heating resorcinol with ammonium chloride and an aqueous solution of ammonia at 200°. Bromination in acetic anhydride yields 2,4,6-tribromo-3-aminophenol, m.p. 119° (Bamberger, Ber. 48, 1354). 2,4-Dinitro-3-aminophenol, m.p. 225° (Bamberger, Ber. 49, 1257). Monoalkyl-*m*-aminophenols, Ger. Pats. 48,151 and 76,419. Dimethyl-*m*-aminophenol,  $\text{C}_6\text{H}_3(\text{OH}) \cdot \text{N}(\text{CH}_3)_2$ , m.p. 87°. Diethyl-*m*-aminophenol, b.p. about 280°. *m*-Aminophenol and its derivatives are used in making rhodamine dyes (*q.v.*). For the action of phosgene on alkylated *m*-aminophenols see Meyenburg, Ber. 29, 501. *m*-Hydroxyphenyl-trimethyl-ammonium hydroxide,  $\text{C}_6\text{H}_4[1]\text{OH}[3]\text{N}(\text{CH}_3)_3\text{OH}$  (Hantzsch, Ber. 29, 1533).

*p*-Aminophenol, m.p. 184° (decomp.), sublimes at its m.p. It is obtained (1) from *p*-nitrophenol; (2) from  $\beta$ -phenylhydroxylamine (p. 69); (3) by electrochemical reduction of nitrobenzene in sulphuric acid solution (Burgham, Am. Electroch. Soc. 61, 1932), due to the rearrangement of  $\beta$ -phenylhydroxylamine first formed; (4) from 5-amino-salicylic acid by loss of carbon dioxide; (5) by heating *p*-chlorophenol with ammonia in presence of copper (Ger. Pat. 205,415); (6) from *p*-amino-alkoxybenzenes by removing the alkyl group by means of 75% sulphuric acid at 160° (Br. Pat. 293,792).

*p*-Aminophenol is used as a photographic developer under the name of *Rodinal* (Ger. Pat. 60,174). It is oxidised by silver oxide to quinone-monoimine (p. 242), and by chromic acid, or lead dioxide and sulphuric acid to quinone. Bleaching powder converts it, and its halogen substitution products into quinone-chlorimines. *p*-Aminophenol reacts in the same way, and as readily as phenylhydrazine, with aldehydes and ketones in dilute acetic acid (Michaelis, Ber. 27, 3005). The bromination of *p*-aminophenol and *p*-aminophenetole has been studied by Fuchs (Mo. 38, 331).

*p*-Methylaminophenol, m.p. 87°, is obtained by heating hydroquinone with methylamine in a sealed tube to 200° (Harger, Am. 41, 270), or by heating *p*-hydroxyphenyl-glycine, when carbon dioxide is eliminated (U. S. Pats. 1,844,844 and 1,844,926). The sulphate, m.p. 250-260°, is the photographic developer *Metol*. *p*-Aminophenol condenses with chloroacetic acid and sodium acetate to *p*-hydroxy-phenylglycine,  $\text{HOC}_6\text{H}_4\text{NHCH}_2\text{COOH}$ , m.p. 220-245°; the nitrile of this acid, m.p. 100°, has been obtained by the action of formaldehyde and sodium bisulphite on *p*-aminophenol, and replacing the sulphonic group in the product with CN (Galatis, Helv. 4, 574). When *p*-aminophenol is condensed with chlorohydrin or glycidol, *N*-dihydroxypropyl-*p*-aminophenol, m.p. 192°, is obtained. The two last-named compounds are photographic developers (Ger. Pats. 343,994 and 345,471).

*p*-Aminophenol ethers are obtained by reduction of *p*-nitrophenol ethers (Spiegel, Ber. 34, 1935), or by a rearrangement of  $\beta$ -phenylhydroxylamine in alcoholic sulphuric acid (Bamberger, Ber. 33, 3602). Methyl ether, *p*-anisidine, b.p. 246°.

*p*-Aminophenyl ether,  $\text{PhOC}_6\text{H}_4\text{NH}_2$ , m.p.  $82^\circ$ , is obtained from *p*-nitrophenyl ether by the action of iron and acetic acid (*Mailhe*, C.r. 154, 1240).

*p*-Aminophenetole, *p*-phenetidine,  $\text{NH}_2[\text{C}_6\text{H}_4[1]\text{OC}_2\text{H}_5]$ , b.p.  $242^\circ$  is converted by boiling acetic acid into *p*-acetaminophenetole,  $\text{CH}_3\text{CONH}[\text{C}_6\text{H}_4[1]\text{OC}_2\text{H}_5]$ , which is known as *phenacetin*, an antipyretic. It is a mixture of two forms, one stable, m.p.  $134\text{--}135^\circ$ , and the other metastable, m.p.  $128\text{--}129^\circ$ . When acted upon by 80–90% sulphuric acid, phenacetin undergoes a remarkable decomposition into ethyl acetate and *p*-aminophenol (*Cohn*, Ann. 309, 233). On prolonged boiling with an excess of acetic anhydride, phenacetin is converted into diacetyl-phenetidin,  $(\text{CH}_3\text{CO})_2\text{NC}_6\text{H}_4\text{OC}_2\text{H}_5$ , m.p.  $54^\circ$ , b.p.  $182^\circ$  (12 mm.). This compound, and *p*-ethoxyphenyl-succinimide, *pyrantin*,  $(\text{CH}_2\text{CO})_2\text{NC}_6\text{H}_4\text{OC}_2\text{H}_5$ , m.p.  $155^\circ$ , have a similar action to phenacetin. Pyrantin is said to be more free of after-effects than phenacetin. *p*-Phenetolecarbamide, *dulcin*,  $\text{NH}_2\text{CO}\cdot\text{NH}[\text{C}_6\text{H}_4[1]\text{OC}_2\text{H}_5]$ , m.p.  $173\text{--}174^\circ$ , is obtained by the action of urea, or carbonyl chloride and ammonia, on *p*-phenetidine, or by heating di-*p*-phenetole-urea with urea, or ammonium carbamate or carbonate. It is difficultly soluble in cold water, but dissolves freely in warm water, and possesses a very sweet taste, about 200 times more sweet than cane sugar (Ger. Pats. 77,310 and 77,420). The effect of substituents on the taste has been investigated by Thoms.

*m*-Hydroxy-diphenylamine,  $\text{PhNH}[\text{C}_6\text{H}_4[1]\text{OH}]$ , m.p.  $82^\circ$ , b.p.  $340^\circ$ , and *p*-hydroxy-diphenylamine, m.p.  $70^\circ$ , b.p.  $330^\circ$ , are prepared by heating resorcinol and hydroquinone with aniline and zinc chloride (*Limpricht*, Ber. 22, 2909; homologues, see *Gnehm*, J. pr. 65, 49). 2,4-Dinitro-4'-hydroxydiphenylamine, red needles, m.p.  $195\text{--}196^\circ$ , is obtained from *p*-aminophenol and 4-chloro-1,3-dinitrobenzene by the action of sodium acetate in boiling alcohol (*Meldola*, J. 111, 546, 551). *p,p*-Dihydroxy-diphenylamine,  $\text{NH}(\text{C}_6\text{H}_4[4]\text{OH})_2$ , m.p.  $174^\circ$ , is obtained from hydroquinone by heating with ammonia or *p*-aminophenol (*Schneider*, Ber. 32, 689). The hydroxy-diphenylamines are closely related to the indophenol dyes (cf. quinones, p. 245). *p,p'*-Amino-hydroxy-diphenylamine,  $\text{NH}_2\text{C}_6\text{H}_4\text{NHC}_6\text{H}_4\text{OH}$ , m.p.  $166^\circ$ , is prepared by reducing the corresponding nitro-compound (*Ullmann*, Ber. 42, 1080), or by oxidising a mixture of *p*-phenylenediamine and phenol with hypochlorite in the presence of a copper salt (Ger. Pat. 204,596). An alkaline solution of *p*-amino-*p*-hydroxy-diphenylamine soon acquires a blue colour due to the formation of indamine (p. 247). *p,p*-Dimethylamino-hydroxy-diphenylamine,  $(\text{CH}_3)_2\text{N}\cdot\text{C}_6\text{H}_4\text{NHC}_6\text{H}_4\text{OH}$ , m.p.  $161^\circ$ , see *Gnehm*, Ber. 35, 3085.

Hydroxyphenyl mustard oils of the para series,  $\text{HO}[\text{C}_6\text{H}_4[1]\text{NCS}]$ , are produced in the same way as the mustard oils (p. 98). *p*-Aminophenol or its ethers are acted upon by ammonia and carbon disulphide, giving ammonium dithiocarbamates,  $\text{Ar}\cdot\text{NH}\cdot\text{CS}_2\cdot\text{NH}_4$ , and these are treated with carbonyl chloride. *p*-Hydroxyphenyl mustard oil, m.p.  $43^\circ$ , anisyl mustard oil, b.p.  $164^\circ$  (37 mm.); phenetyl mustard oil, m.p.  $62^\circ$  (*Slotta*, Ber. 63, 888).

**DIAMINOPHENOLS.** 2,4-Diaminophenol,  $(\text{NH}_2)_2[\text{C}_6\text{H}_3[1]\text{OH}]$  is obtained from 2,4-dinitrophenol by catalytic hydrogenation under pressure, or from *m*-dinitrobenzene or *m*-nitraniline by electrolytic reduction in sulphuric acid (*Gattermann*, Ber. 26, 1348). The free base is very unstable. Its salts are used under the name *amidol* as developers in photography. 4,5- and 2,5-Diaminophenols are prepared from nitro-amino-phenols obtained by the action of sulphuric acid on *o*- and *p*-nitro-diazo-imides (p. 133) (*Kehrmann*, Ber. 30, 2096; 31,

2403). The formation of *m*-anilido-*p*-phenetidine,  $\text{C}_6\text{H}_5\text{NH}[\text{C}_6\text{H}_4] \begin{matrix} \text{OC}_2\text{H}_5[1] \\ \text{NH}_2[4] \end{matrix}$ ,

is dealt with below with the hydrazine-phenols.

Picramic acid, 2-amino-4,6-dinitrophenol,  $(\text{NH}_2)(\text{NO}_2)_2\text{C}_6\text{H}_2\text{OH}$ , m.p.  $165^\circ$ , consists of fine red needles, and is prepared by reducing picric acid with alcoholic ammonium sulphide, or with sodium hydrosulphite. For other dinitro-*p*-amino-phenols see *Reverdin*, Ber. 38, 1593.

2,4,6-Triaminophenol,  $(\text{NH}_2)_3\text{C}_6\text{H}_2\text{OH}$ , is produced by the action of phosphorus triiodide, or of tin and hydrochloric acid on picric acid (*Bamberger*, Ber. 16, 2400), and also by the reduction of phenol-trisazo-benzene (p. 211). When liberated from its salts it decomposes rapidly. It forms salts which crystallise well with three equivalents of acid. The hydriodide,  $\text{C}_6\text{H}_2\text{OH}(\text{NH}_2)_3\cdot 3\text{HI}$ , crystallises in colourless needles. Solutions of the salts when made weakly alkali-

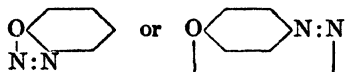


line show a beautiful blue colour. When ferric chloride is added to a solution of the hydrochloride, a deep-blue colour appears, and brownish-blue needles with a metallic lustre separate. These are *amino-diimino-phenol* or *diamino-quinonimine* hydrochloride (p. 244). They dissolve in water with a beautiful blue colour. An isomeric triaminophenol has been obtained by the reduction of diquinoyl-trioxime (*Nietzki*, Ber. 30, 183). 2,3,4,5-Tetramino-anisole,  $(\text{NH}_2)_4\text{C}_6\text{HOCH}_3$  (*Nietzki*, Ber. 25, 282).

**DIAZOPHENOLS.** Phenol-diazonium chlorides,  $\text{HO}\cdot\text{C}_6\text{H}_4\text{N}_2\text{Cl}$ , are obtained by the action of nitrous acid on the hydrochlorides of aminophenols. In the salts of polyhalogeno-, polynitro-, and polysulphonated diazonium bases with weak acids, such as acetates, and carbonates, hydroxyl groups can readily be introduced, displacing an *o*- or *p*-halogen, nitroyl, or sulphonyl group. In this way substituted diazophenols have been obtained (*Hantzsch*, Ber. 36, 2069; *Noelting*, Ber. 39, 79; *Orton*, J. 83, 796; 91, 1554). The free diazohydrates of *o*- and *p*-aminophenols anhydridise, and yellow so-called "quinone-diazides" are formed, probably owing to a rearrangement to a quinoid form (cf. the formula of diazomethane, Vol. I, p. 251, and this vol., p. 116, and *Hantzsch*, Ber. 35, 888):



*o*- and *p*-Diazophenols have also been formulated as internal diazo-oxides:



(*Morgan*, J. 107, 645), but these cyclic formulae are rather improbable, at any rate for the *p*-compound; cf. p. 178. A formulation as a diazonium-betaine,  $-\text{O}-\text{C}_6\text{H}_4\text{N}_2^+$ , might also be possible. It differs from the quinone-diazide formula only in the distribution of electrons. The true structure might be one intermediate between these two formulae. However, colour, melting points, and solubilities point to a constitution very nearly approaching the diazide state.

The sulphonic acids of *m*-aminophenols form internal diazonium sulphonates,  $\text{HO}[1]\text{C}_6\text{H}_3\begin{matrix} \swarrow \text{N}_2[3]^+ \\ \searrow \text{SO}_3[4]^- \end{matrix}$ , which do not give diazo-oxides with bases as the *p*-compounds do, but lose nitrogen and break down into derivatives of resorcinol-sulphonic acid. These latter give azo-dyes with the unchanged diazonium sulphate (*Morgan*, J. 111, 497).

*p*-Diazobenzene cyanide,  $\text{HO}[4]\text{C}_6\text{H}_4\text{N}_2\cdot\text{CN}$ , small yellow needles, obtained by the action of potassium cyanide on the chloride, is hydrolysed by caustic potash to potassium diazophenol-carboxylate,  $\text{HOC}_6\text{H}_4\text{N}_2\text{COOK}$ .

Dibromo-diazophenol,  $\text{Br}_2[4,6]\text{C}_6\text{H}_2(\text{O})(\text{N}_2)[1,2]$ , orange-yellow prisms, m. p.  $130^\circ$  (decomp.) (*Bamberger*, Ber. 39, 4248). Dibromophenol-diazosulphonic acid,  $\text{C}_6\text{H}_2\text{Br}_2(\text{OH})\text{N}_2\text{SO}_3\text{H} + 2\text{H}_2\text{O}$ , is obtained from its potassium salt, which is itself obtained by the action of potassium sulphite on dibromophenol-diazo chloride.

*p*-Phenol-diazomercaptan hydrosulphide,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{N}_2\text{SH}\cdot\text{H}_2\text{S}$ , forms red needles, m. p.  $75^\circ$  (decomp.), and is obtained by the action of hydrogen sulphide on solutions of diazophenol salts (*Hantzsch*, Ber. 28, 3250).

*p*-Hydroxy-diazobenzene-imide,  $\text{OH}[1]\text{C}_6\text{H}_3[4]\text{N}_2$ , m. p. about  $20^\circ$ , explodes on heating to  $150^\circ$ . It is obtained from *p*-aminophenol and nitrous acid. Its potassium compound exists in two forms, one colourless, the other blue, which are readily converted into one another. Both give the same benzoyl compound, m. p.  $81^\circ$ , which is also obtained from benzoyl-*p*-aminophenol by the action of nitrous acid (*Forster*, J. 91, 855).

**AZOXY-PHENOLS.** The asymmetrically substituted azoxy-phenols form two series of isomers which are formulated in an analogous manner to the isomeric azoxy-benzenes by *Angeli* (p. 134). *p*-Hydroxy-azoxybenzene,  $\alpha$ -form,  $\text{Ph}\cdot\text{N}(\text{O})\text{:N}\cdot\text{C}_6\text{H}_4\text{OH}$ , m. p.  $156^\circ$ ,  $\beta$ -form,  $\text{Ph}\cdot\text{N:N}(\text{O})\cdot\text{C}_6\text{H}_4\text{OH}$ , m. p.  $117^\circ$ , are both formed when *p*-hydroxy-azobenzene is oxidised with hydrogen peroxide (*Angeli*, *Lincoi* 23, II, 31). The  $\alpha$ -form is also obtained by condensing *p*-nitrosophenol and  $\beta$ -phenylhydrosulphide, water being eliminated, or, together with two iso-

meric *o*-hydroxy-azoxybenzenes, m.p. 76° and 108°, by the action of caustic soda on nitrosobenzene at 100°. The  $\beta$ -form is unaffected by potassium permanganate, but the  $\alpha$ -form is readily oxidised (*Angeli*, *Lincei* 32, I, 443, 539), producing potassium benzene isodiazotate (*Bamberger*, *Ber.* 35, 1614):  $\text{Ph}(\text{N}_2\text{O})\text{C}_6\text{H}_4\text{OH} \rightarrow \text{PhN}_2\text{OK}$  (p. 120). *p*-Ethoxy-azoxybenzenes (*p*-azoxy-phenetoles). When *p*-ethoxy-azobenzene is oxidised in acetic acid solution with hydrogen peroxide, two isomers are formed which can be separated by solution in ligroin. The  $\alpha$ -form is sparingly soluble,  $\text{Ph}\cdot\text{N}(\text{O})\text{:N}\cdot\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$ , m.p. 72°, whilst the  $\beta$ -form is more readily soluble,  $\text{Ph}\cdot\text{N:N}(\text{O})\cdot\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$ , m.p. 56°. The azo-compound is re-formed on reduction (*Angeli*, *Lincei* 21, I, 729). *p*-Azoxy-phenetole, and *p*-azoxy-anisole, m.p. 91° and 97–98°, have been obtained in the liquid-crystalline form (*Mauguin*, *C.r.* 152, 1680; *Deitsch*, *Z. Krystall.* 50, 24; *Lehmann*, *Ann. Phys.* 48, 177).

**AZOPHENOLS. HYDROXY-AZOBENZENES. Formation:—1.** By the action of diazonium salts on monohydric phenols or their ethers, *m*-dihydroxy-benzenes or their ethers, *m*-aminophenols, *m*-phenol sulphonic acids, or phenol-carboxylic acids (*Grandmougin*, *Ber.* 40, 3450):

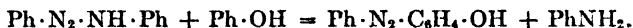


The diazonium solution is allowed to run into an alkaline solution of the phenol (or derivative) with stirring and cooling. According to the conditions and proportions, phenol-azobenzene, *o,p*-phenol-bisazobenzene, *o,o,p*-phenol-trisazobenzene, are formed. When an *o*-position relative to the OH-group is unoccupied, *o,p*-disazo-phenols are formed as by-products. When the *o*- and *p*-positions are occupied, coupling may still take place by addition. The greater the number of alkyl groups in a phenol or phenol ether, the more readily will it couple with diazo-compounds, alkyl groups in the *m*-position being the most effective (*Meyer*, *Ber.* 47, 1741; *Auwers*, *Ber.* 47, 1275; 48, 1716; *Charrier*, *Gazz.* 44, II, 503; *Pured-du*, *Gazz.* 46, I, 211). An aqueous solution of phenol and diazonium sulphate react to give phenyl ether. As in the case of the amino-azo-compounds, the diazo-group which enters the phenol prefers the *p*-position relative to hydroxyl; and if this position is occupied, the ortho (*Liebermann*, *Ber.* 17, 876; *Ger. Pat.* 44,906). *o*-Hydroxy-azo-compounds can be obtained by coupling diazonium compounds with *p*-acetamino-phenols and then eliminating the acetamino group (*Hewitt*, *J.* 101, 1765).

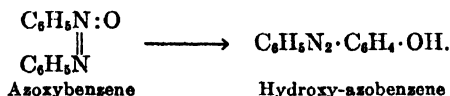
In some cases it has been possible to isolate intermediate products in these reactions. These are the so-called O-azo compounds or diazo-oxy-benzenes, which are analogous to the diazoamino-compounds and undergo a similar rearrangement to the latter, with the formation of hydroxy-azo-compounds (*Dimroth*, *Ber.* 41, 4016; *Auwers*, *Ber.* 41, 4304):



2. From diazoaminobenzenes and monohydric phenols, or resorcinol, on heating (*Heumann*, *Ber.* 20, 372, 904; *Fischer*, *ibid.*, 1577):



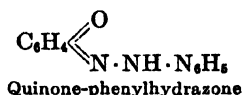
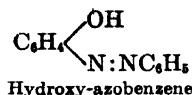
By the molecular rearrangement of azoxy-benzenes on heating with sulphuric acid (*Wallach*, *Ber.* 14, 2617):



4. From nitrophenols by reduction with alcoholic potash. 5. By the action of anilines on nitroso-phenols. 6. From amino-azobenzenes, and from azobenzene sulphonic acids.

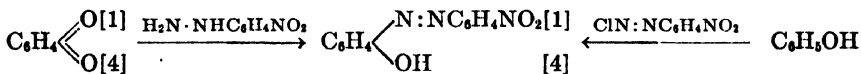
The hydroxyazo-compounds, like the nitroso-phenols (p. 202), may be formu-

lated in two ways. They may have the "normal" constitution, and that of quinone-phenylhydrazones (*Burawoy*, Ann. 509, 60):



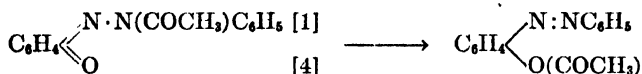
Alkyl- and acyl-derivatives derived from both forms are known. O- and N-alkyl-derivatives are known in both the *o*- and *p*-series, but O- and N-acyl-derivatives are known in the *p*-series only. In the *o*-series, the acyl group is always attached to oxygen (*Auwers*, Ann. 487, 80; *cf.*, however, *McPherson*, Am. 31, 281).

Attempts to prepare quinone-phenylhydrazone itself by condensing benzoquinone with phenylhydrazine have not been successful, as quinone is reduced by phenylhydrazine. With *o*-nitro- and *o,p*-dinitro-phenylhydrazines, however, monophenylhydrazones of quinone have been obtained, and these have been proved to be identical with the nitro-hydroxyazo-compounds obtained by coupling phenol with diazotised *o*-nitro- and *o,p*-dinitro-anilines, respectively (*Borsche*, Ann. 357, 171; *cf.* naphthaquinone-hydrazones, p. 631):



*as*-Acetyl- and *as*-benzoyl-phenylhydrazines, like quinone, give N-acylated quinone-phenylhydrazones (p. 244), which hydrolyse to *p*-hydroxy-azobenzene, and are isomeric with the O-acyl-hydroxy-azobenzenes obtained by acetylation or benzoylation of hydroxy-azobenzene (*McPherson*, Am. Ch. J. 22, 364).

N-Acylated *p*-quinone-phenylhydrazones change with great ease into the isomeric O-acetylated hydroxy-azobenzenes (*Willstätter*, Ber. 40, 1432):



A migration of the acyl-group in the opposite direction, from oxygen to nitrogen, has been observed in reducing acetylated benzene azo-*p*-cresol, but not with the benzoylated compound (*Auwers*, Ber. 47, 1297).

On the evidence of this ready transition of quinone phenylhydrazone derivatives into hydroxy-azobenzene derivatives (for the converse rearrangement of the mixed azo-compounds, see p. 138), the free *o*- and *p*-hydroxy-azo compounds have been regarded as true azo-compounds. In support of this, it has been pointed out that the general behaviour of *m*-hydroxy-azobenzene (see above) is very similar to that of the *o*- and *p*-isomers, and that the *m*-isomer could not be formulated as a quinone-phenylhydrazone, since *m*-quinones do not exist (p. 233).

*o*- and *p*-Hydroxy-azobenzenes combine with phenyl isocyanate forming O-carbanilido-derivatives,  $\text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{N} \cdot \text{NC}_6\text{H}_5 \\ \diagdown \text{OCONHC}_6\text{H}_5 \end{array}$  (*Goldschmidt*, Ber. 38, 1098). The

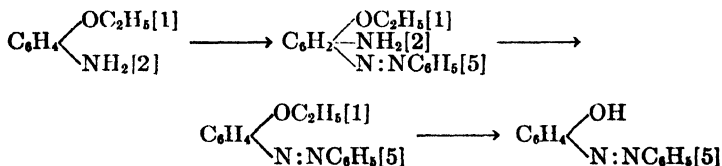
fact that the *o*-hydroxy-azo compounds are insoluble or difficultly soluble in alkalis has been regarded as a strong argument in favour of their quinoid structure. The phenylhydrazones of *o*-phenol-aldehydes and *o*-phenol-ketones, are however, insoluble (*Anselmino*, Ber. 35, 4100; *Jacobson*, Ber. 36, 4118; *Torrey*, Am. 30, 836; *Puxeddu*, Gazz. 51, I, 256). There is general agreement at present for formulating the *p*-, and of course, the *m*-hydroxy-azobenzenes as true azo-phenols, but important objections have been raised against a similar formulation of the *o*-compounds. The absorption spectrum of the *o*-compound is in favour of a quinone-phenylhydrazone constitution (*Burawoy*, Ann. 503, 180; 509, 60; *cf.* *Auwers*, Ann. 505, 283).

*p*-Hydroxy-azobenzene, benzene-*p*-azophenol,  $\text{PhN}=\text{N}[1]\text{C}_6\text{H}_4[4]\text{OH}$ , m.p. 151–153°, crystallises in orange-yellow needles. It is obtained by the general

methods given for the formation of hydroxy-azo-compounds. On treatment first with phosphorus pentachloride and then with water, it gives the phosphoric ester  $\text{PO}(\text{OC}_6\text{H}_4\text{N}_2\text{Ph})_2$ , m.p.  $148^\circ$  (Bamberger, Ber. 35, 1622). Electrochemical reduction in alcoholic hydrochloric acid gives *p*-aminophenol (Puxeddu, Gazz. 48, II, 25). Two forms are known, possibly stereoisomers. On nitration the  $\alpha$ - (*trans*?) form yields a tetranitro-derivative, and the  $\beta$ - (*cis*?) form a dinitro-derivative (J. 103, 1472, 1479). Benzene-azo-*p*-phenetole, m.p.  $77^\circ$  (Jacobson, Ber. 25, 994). *p*-Azophenol,  $\text{HO}[4]\text{C}_6\text{H}_4[1]\text{N}_2[1]\text{C}_6\text{H}_4\text{OH}$ , m.p.  $204^\circ$ , light-brown crystals, is obtained from *p*-nitro- and *p*-nitroso-phenol by fusion with potash, by coupling hydroxyphenyl-diazonium nitrate with phenol, and from *p*-hydroxy-azobenzene sulphonic acid. It forms a double compound with 2 mols. of nitrous acid, m.p.  $75^\circ$ , when treated with the latter in a cold mixture of alcohol and ether (Charrier, Gazz. 44, I, 405).

*o*-Hydroxy-azobenzene, m.p.  $83^\circ$ , is readily volatile with steam, in contrast with the *p*-derivative. It is obtained by coupling phenyl-diazonium salts with phenol (Bamberger, Ber. 33, 3189), together with a much greater quantity of the *p*-compound. It is also formed by coupling phenyl-diazonium chloride with *p*-acetamino-phenol, removing the acetyl group and eliminating  $\text{NH}_3$  by Sandmeyer's method (Worostizov, J. Russ. Phys. Chem. Soc. 43, 787) or by the rearrangement of azoxy-benzene (Lachmann, Ann. 24, 1178; Knipscher, Rec. 22, 1). It is obtained along with hydroxy-azoxy-benzenes and other substances by the action of caustic soda on nitrosobenzene. Its methyl ether, benzeneazo-*o*-anisole, m.p.  $41^\circ$  has been synthesised from *o*-anisidine and nitrosobenzene, and also yields *o*-hydroxy-azo-benzene when treated with aluminium chloride (Bamberger, Ber. 33, 3189).

*m*-Hydroxy-azobenzene, m.p.  $114$ – $117^\circ$ , canary-yellow crystals, has been prepared by Jacobson (Ber. 36, 4102), by coupling *o*-amino-phenetole with phenyl-diazonium chloride, removing the amino-group, and hydrolysing the resulting benzene-azo-*m*-phenetole, m.p.  $64^\circ$ , with aluminium chloride:

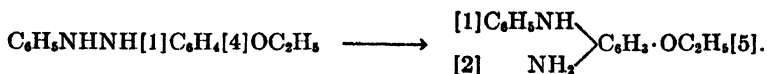


*m,m'*-Dihydroxy-azobenzene, *m*-azophenol, m.p.  $205^\circ$ , is formed by the fusion of *m*-nitrophenol with caustic potash, and has also been obtained from *m*-azoaniline (p. 143) by means of the diazo-compound, and by the electrolytic reduction of *m*-nitrophenol (Elbs, J. pr. 67, 265). For azo- and diazo-compounds of the cresols see Noetting, Ber. 17, 351.

The sulphonic acids of the hydroxy-azobenzenes are dyes. *p*-Sulphobenzene-*p*-azophenol,  $\text{SO}_3\text{H}[4]\text{C}_6\text{H}_4[1]\text{N}=\text{N}[1]\text{C}_6\text{H}_4[4]\text{OH}$ , for instance, obtained by the action of sulphuric acid on *p*-hydroxy-azobenzene, or by the action of sodium phenate on *p*-diazobenzene sulphonic acid, is the commercial dye *tropaeolin Y* (Griess, Ber. 11, 2192). Cf. also resorcinol. Phenol-2,4-bisazobenzene,  $\text{OH}[1]\text{C}_6\text{H}_3[2,4](\text{N}:\text{NPh})_2$ , m.p.  $123^\circ$  (Vignon, C.r. 138, 1278), and phenol-2,4,6-tris-azobenzene,  $\text{OH}[1]\text{C}_6\text{H}_3[2,4,6](\text{N}:\text{NPh})_3$ , m.p.  $215^\circ$ , are formed by coupling phenol with 2 and 3 molecules, respectively, of phenyl-diazonium chloride in alkaline solution. Phenol-trisazobenzene is reduced to 2,4,6-triaminophenol by tin and hydrochloric acid (p. 207) (Grandmougin, J. pr. 78, 384).

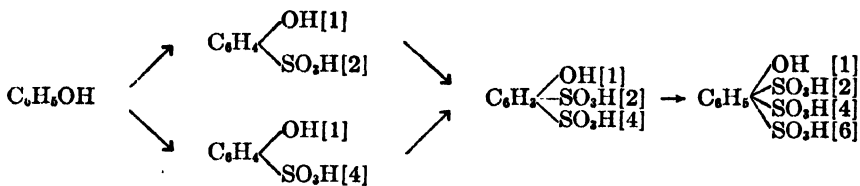
**HYDRAZOPHENOLS.** *m*-Hydroxy-hydrazobenzene,  $\text{OH}[1]\text{C}_6\text{H}_4[3]\text{NH}\cdot\cdot\text{NHPh}$ , colourless needles, m.p.  $126^\circ$ , is obtained by the reduction of *m*-hydroxy-azobenzene with zinc dust and acetic acid (Jacobson, Ber. 36, 4112). Under the influence of mineral acids it rearranges to *m*-hydroxybenzidine. It is the only known free hydroxy-hydrazo compound, since *o*- and *p*-hydroxy-azobenzenes, when reduced, immediately decompose into aniline and *o*- or *p*-aminophenol. The alkyl ethers of hydroxy-azobenzenes can, however, be reduced to ethers of benzene-*o*- and benzene-*p*-hydrazophenol ethers. The benzene-*p*-hydrazophenol ethers undergo the semidine transformation on treatment with  $\text{SnCl}_2$  and  $\text{HCl}$  (p. 145),

e.g., benzene-*p*-hydrazophenetole is converted into *m*-ethoxy-*o*-amino-diphenylamine (Jacobson, Ber. 27, 2700; 29, 2680; Ann. 287, 97):



The free hydrazine-phenols are very unstable. *o*-Hydrazine-anisole,  $\text{NH}_2\text{NH}-[2]\text{C}_6\text{H}_4[1]\text{OCH}_3$ , m.p. 43°, b.p. 240° (Reisenegger, Ann. 221, 314).

**PHENOL SULPHONIC ACIDS.** When phenol is sulphonated, the *o*- and *p*-hydrogen atoms are replaced by  $\text{SO}_3\text{H}$  groups, just as in nitration it is the *o*- and *p*-atoms that are concerned. The sulphonic groups take up positions *m*- to each other:

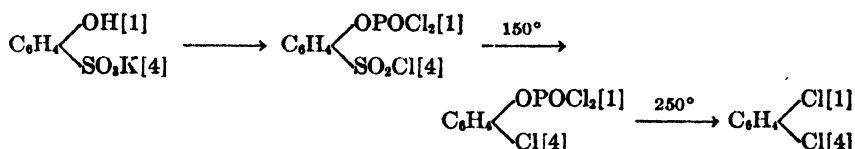


*o*- and *p*-Phenol sulphonic acids are formed when phenol is dissolved in concentrated sulphuric acid. At moderate temperatures the former predominates, but readily passes into the *p*-acid when heated with concentrated sulphuric acid. This change is due to the fact that *o*-phenol sulphonic acid readily gives up its sulphonic acid group with re-formation of phenol, which then forms the *p*-acid under the action of sulphuric acid. *o*-Phenetole sulphonic acid is similarly readily converted into the *p*-acid on heating to 100° (Moody, Proc. 1892-1893, 214). Phenol sulphonic acids or their ethers, are also formed from phenols or their ethers, when they are heated with dimethyl sulphate in the absence of water and alkali (Simon, C.r. 176, 900).

The separation of *o*- and *p*-phenol sulphonic acids is effected by the crystallisation of their mono-barium salts. The barium salt of the *o*-acid,  $[\text{C}_6\text{H}_4(\text{OH})\text{SO}_3]_2\cdot\text{Ba}\cdot\text{H}_2\text{O}$  separates first in compact rhombic needles. The *p*-acid remains in the mother liquor, and is best separated as its magnesium salt,  $[\text{C}_6\text{H}_4(\text{OH})\text{SO}_3]_2\cdot\text{Mg}\cdot 8\text{H}_2\text{O}$ , large rhombic columns (Obermiller, Ber. 40, 3637). The *p*-acid is also formed by the rearrangement of phenyl-sulphuric acid (p. 195). The free acids crystallise when their aqueous solutions are allowed to evaporate slowly. The *p*-acid gives quinone when its sodium salt is heated with manganese dioxide and sulphuric acid. The *o*-acid gives catechol when fused with caustic potash at 310°, while the *p*-acid is not attacked below 320°, and at higher temperatures gives diphenols (see diphenyl). By the action of nitric acid the sulphonic acid group is readily displaced by the nitro-group.

*p*-Phenol sulphonic acid has been converted by a process known as "depsidation" (p. 368), into polymolecular sulphonic acids of the type  $\text{HO}\cdot\text{C}_6\text{H}_4\text{SO}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\text{SO}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\text{SO}_3\cdot\text{Na}$ . These tan hides and are used as *artificial tannins*. Phenol sulphonic acids and formaldehyde condense to give the so-called *neradols* or *synthanes*, which are also tannins (Apostolo, Ger. Pat. 262,558).

On treatment with phosphorus pentachloride, the phenol-sulphonic acids give phosphorus oxychloride derivatives of phenol sulphonyl chlorides as the primary products. When these are heated with phosphorus pentachloride to 150°, they are converted into chlorophenols, and at a still higher temperature into chlorobenzene (Anschütz, Ann. 415, 64).



The position of the sulphonyl group can be determined by a consideration of these reactions (*Kekulé*, Ber. 6, 943; *Anschtütz*, Ann. 358, 92). If phenol sulphonyl chlorides are required in preparations, potassium phenol sulphonates are acetylated, the chlorides of the acetyl-phenol sulphonic acids are prepared, and the acetyl group is removed after the reaction (*Anschtütz*, Ber. 45, 2378; Ann. 415, 51).

When ammonia or, better, diethylamine, acts on acetyl-*o*-phenol sulphonyl chloride in ether, the constituents of acetyl chloride are lost and a compound is obtained which is also formed by the action of phosphorus pentoxide or oleum on phenol-*o*-sulphonic acids, or by the action of phosphorus oxychloride on the acids or their alkali salts.

This compound is phenylene-sulphonylide,  $\text{C}_6\text{H}_4 \begin{matrix} \diagup \text{O} \text{---} \text{SO}_2 \diagdown \\ \diagdown \text{SO}_2 \text{---} \text{O} \diagup \end{matrix} \text{C}_6\text{H}_4$ , m.p.  $237^\circ$ , corresponding, as the name implies, to  $\alpha$ -disulicylide. Sodium hydroxide reconverts it into *o*-phenol sulphonic acid. Sulphonides of the homologous phenols have also been prepared (*Anschtütz*, Ann. 415, 64 *et seq.*).

On iodination, the *p*-sulphonic acid gives 1,6-diiodo-*p*-phenol sulphonic acid,  $\text{C}_6\text{H}_2\text{I}_2(\text{OH})\cdot\text{SO}_3\text{H}$ , which is used as an antiseptic under the name of *Sozoiodol*.

*m*-Phenol sulphonic acid is formed by heating *m*-benzene disulphonic acid (p. 176) at  $170$ – $180^\circ$  with caustic potash (*Barth*, Ber. 9, 969). The free acid contains 2 mols. of water. When fused with potash it is converted into resorcinol at a temperature as low as  $250^\circ$ . When *p*-benzene-disulphonic acid is heated with caustic potash, the same substances are formed, first *m*-phenol sulphonic acid, and then resorcinol. For *p*-phenol sulphonic acid and its reaction products with phosphorus pentachloride, see *Anschtütz*, Ann. 415, 51.

Phenol-2,4-disulphonic acid is obtained from phenol or *o*- or *p*-phenol sulphonic acids by sulphonation, according to the scheme given above. Its solution gives a dark red colour with ferric chloride.

Phenol-2,4,6-trisulphonic acid, obtained by the action of concentrated sulphuric acid and phosphorus pentoxide on phenol, crystallises with 3 mols. of water in prisms.

For nitrophenol sulphonic acids, see *King*, J. 119, 2105.

*p*-Aminophenol sulphonic acid,  $\text{NH}_2[4]\text{C}_6\text{H}_3\text{OH}[1]\text{SO}_3\text{H}[2]$ , is formed in small yield by the action of concentrated sulphuric acid on nitrobenzene, which is presumably first reduced to  $\beta$ -phenylhydroxylamine, then rearranged, under the influence of sulphuric acid to *p*-aminophenol, and finally sulphonated (*Brunner*, C. 1908, II, 587). For other aminophenol sulphonic acids, see *Noyes*, Am. Ch. J. 16, 511; *Schultz*, Ber. 39, 3345; Ger. Pats. 79,120 and 150,982.

### Sulphur Derivatives of Phenol

**MERCAPTANS.** Thiophenol, *phenyl-mercaptan*,  $\text{C}_6\text{H}_5\text{SH}$ , b.p.  $169^\circ$ ,  $d_4^{15}$  1.078, is a mobile, evil-smelling liquid. It is obtained: (1) by the action of  $\text{P}_2\text{S}_5$  on phenol (*Kekulé*, Z. f. Ch. 1867, 193); (2) by the action of KHS on sodium benzene sulphonate (*Stadler*, Ber. 17, 2080); (3) by the action of zinc and sulphuric acid, or of stannous chloride on benzene sulphonyl chloride, or benzene sulphonic acid (*Bourgeois*, Rec. 18, 426; *Gattermann*, Ber. 32, 1147; *Winter*, Am. Ch. J. 31, 572); (4) from ethyl-phenyl-dithiocarbonate (see below); (5) by the action of sulphur on phenyl magnesium bromide; the compound  $\text{PhSMgBr}$  is

first formed, and is then decomposed by acids with the formation of thiophenol (*Taboury*, Ann. ch. ph. 15, 5; *Wuyts*, Bull. 5, 405); (6) by heating phenyl halides with hydrogen sulphide at 700°, with the aid of catalysts (Ger. Pat. 497,570).

Thiophenol tends to change into diphenyl-disulphide, giving off two hydrogen atoms, and therefore acts as a reducing agent (*Troege*r, J. pr. 53, 478). With chlorine it gives phenyl-sulphochloride (p. 182) (*Lecher*, Ber. 58, 409). Thioanisole,  $\text{PhSCH}_3$ , b.p. 190°, is obtained by the action of dimethyl sulphate on thiophenol (*van Hove*, Bull. Belg. 12, 1927). Mercury thiophenate,  $(\text{PhS})_2\text{Hg}$ . Acetyl-thiophenol,  $\text{PhSCOMe}$ , b.p. 231°; thiophenol-acetal,  $(\text{PhS})\text{CH}_2\text{CH}(\text{OEt})_2$ , b.p. 273°; thiophenyl-acetone, m.p. 34°, b.p. 266° (*Authenrieth*, Ber. 24, 163). For mercaptal and mercaptol derivatives of phenol, see *Otto*, Ber. 24, 234; 28, 1120; *Fromm*, Ann. 253, 161.

Phenyl-*o*-thioformate,  $\text{CH}(\text{SPh})_2$ , m.p. 39° (*Laves*, Ber. 25, 347, 361). Ethyl phenyl thiocarbonate,  $\text{PhS}\cdot\text{COOC}_2\text{H}_5$ , m.p. 6°, b.p. 260° (*Otto*, Ber. 19, 1228). Ethyl phenyl dithiocarbonate,  $\text{PhS}\cdot\text{CSOC}_2\text{H}_5$ , is obtained by the action of potassium xanthogenate on phenyl diazonium chloride. This is a general reaction (*C. 1900*, I, 252). It hydrolyses to thiophenol. Next to the reduction of the sulphinic acids (*q.v.*) this is the most convenient method of preparing thiophenols. Phenyl trithiocarbonate,  $\text{CS}(\text{SPh})_2$ , obtained by slowly adding diazotised aniline to potassium thiocarbonate solution is decomposed on heating to carbon disulphide, hydrogen sulphide, and diphenyl-disulphide (p. 215), which can be distilled off (*Casolari*, Gazz. 40, II, 389). Phenyl-*o*-thiocarbonate,  $\text{C}(\text{SPh})_2$ , m.p. 159°, is obtained by the action of thiophenol on the dinitroso-derivative of phenyl-iso-thiourea (*Arndt*, Ann. 396, 17). Phenyl thiocarbonyl chloride,  $\text{PhS}\cdot\text{COCl}$ , b.p. 104° (13 mm.), and phenyl thiocarbonyl chloride,  $\text{PhS}\cdot\text{CSCl}$ , b.p. 135° (15 mm.), are obtained by the action of phosgene and thiophosgene on sodium thiophenate. Numerous derivatives of thiophenol have been prepared from these two compounds by acting on them with alcohol, phenol, thiophenol, aniline, *etc.* (*Rivier*, Bull. 1, 733). Thiophenol and its homologues combine with oxalyl chloride to form thiophenyl oxalic ester chlorides,  $\text{Ph}\cdot\text{S}\cdot\text{CO}\cdot\text{COCl}$ ; when treated with aluminium chloride these lose  $\text{HCl}$  and undergo ring closure to form *thionaphthenes* (Vol. IV), (Ger. Pat. 291,793). Diazobenzene thiophenyl ether,  $\text{PhN}_2\cdot\text{SPh}$ , is an oil, obtained by the action of phenyl diazonium chloride on phenyl mercaptan (*Hantzsch*, Ber. 28, 3237).

*o*-Thiocresol, m.p. 15°, b.p. 188°; *m*-compound, a liquid, b.p. 195–202°; *p*-compound, m.p. 43°, b.p. 194° (*Rabaut*, Bull. [3], 27, 690; *Zincke*, Ber. 43, 837). Thiocarvacrol,  $(\text{CH}_3)(\text{C}_6\text{H}_7)\text{C}_6\text{H}_4\text{SH}$ , b.p. 235°, see carvacrol, p. 190. For other thiophenols see *Gattermann*, Ber. 32, 1147; *Taboury*, Ann. ch. ph. 15, 5.

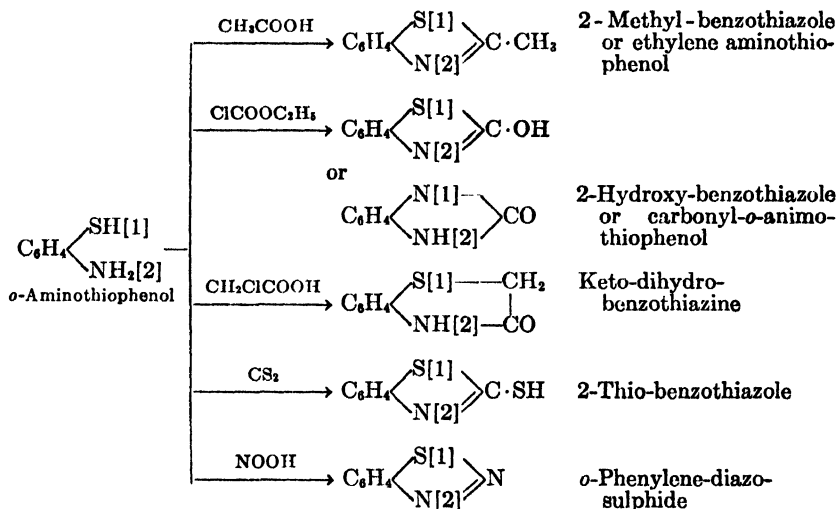
*o*-Nitrothiophenol,  $\text{NO}_2[2]\text{C}_6\text{H}_4\text{SH}$ , m.p. 45°, is easily prepared from *o*-nitrochloro-benzene by the action of sodium sulphide; it is readily oxidised to a disulphide,  $(\text{NO}_2[2]\text{C}_6\text{H}_4)_2\text{S}_2$ , m.p. 198°, which is also obtained by the action of sodium sulphide on *o*-dinitrobenzene, and by the action of alkali polysulphides on *o*-nitrochloro-benzene. *p*-Nitrochloro-benzene gives similarly *p*-nitrophenyl disulphide. When these disulphides are oxidised with nitric acid, the corresponding nitrobenzene sulphonic acids are obtained (*Wohlfahrt*, J. pr. 66, 551). The action of sulphur chloride,  $\text{SCl}_2$ , on *o*-nitrothiophenol gives a sulphur analogue of the aromatic diazo-compounds:  $\text{NO}_2[1]\text{C}_6\text{H}_4[2]\text{S}\cdot\text{S}\cdot\text{Cl}$ , m.p. 62–63° (*Lecher*, Ber. 54, 2249).

Among the substitution products of thiophenol, *o*-aminothiophenol should be noted on account of its heterocyclic condensation products. *o*-Amino-aryl-mercaptans are prepared by treating aromatic amines first with sulphur chloride,  $\text{S}_2\text{Cl}_2$ , and then with alkalis. They react with chloroacetic acid to give *o*-amino-aryl-thioglycollic acids,  $\text{NH}_2\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\text{COOH}$ , or their anhydrides,  $\text{NHC}_6\text{H}_4\cdot\text{SCH}_2\text{CO}$ , m.p. 206° (Ger. Pats. 364,822 and 367,346).

*o*-Amino-thiophenol,  $\text{NH}_2[2]\text{C}_6\text{H}_4[1]\text{SH}$ , m.p. 26°, b.p. 234°, is obtained from the chloride of *o*-nitrobenzene sulphonic acid by reduction with tin and hydrochloric acid, or, more conveniently, by fusing benzenyl-*o*-aminothiophenol with caustic potash (*Hofmann*, Ber. 20, 2259). *m*-Aminothiophenol (*Hofmann*, Ber. 37, 2816). *p*-Aminothiophenol, m.p. 46°, is obtained by the reduction of acetosulphanilic chloride (*Zincke*, Ber. 42, 3362).

**CONDENSATIONS OF THE *o*-AMINOTHIOPHENOLS.** (*Cf. o*-diamines, p. 106, and *o*-aminophenols, p. 204). (1) *o*-Aminothiophenol gives benzo-

*thiazoles* on heating with carboxylic acids or their chlorides or anhydrides. (2) It is converted into 2-hydroxy-benzothiazole or carbonyl-aminothiophenol by the action of chloroformic ester. (3) It gives keto-dihydro-benzothiazine with chloro- or bromoacetic acid. (4) It gives 2-thio-benzothiazole with carbon disulphide. (5) Nitrous acid converts it into *o*-phenylene-diazo-sulphide, which, on heating to 200–220°, is converted into diphenylene disulphide (p. 222):



The condensation of *o*-aminothiophenol with catechol to give *thio-diphenylamine* will be dealt with on p. 221.

**SULPHIDES.** Diphenyl disulphide,  $(\text{C}_6\text{H}_5)_2\text{S}_2$ , m.p. 61°, b.p. 310°, is easily obtained by the oxidation of thiophenol with chromic acid, or in ammoniacal solution simply by the action of air. It is also obtained by the action of iodine on sodium thiophenolate, by heating thiophenol with benzene sulphinic acid, by heating thiophenol or phenyl sulphide with sulphur, from diazo-compounds by the action of polysulphides (Br. Pat. 279,136), etc. Nitro-halogeno-benzenes, such as 1-chloro-2,4-dinitrobenzene, will form disulphides, as well as sulphides and mercaptans, with particular readiness (*Giusa*, Gazz. 53, 341). Reducing agents decompose diphenyl disulphide into two molecules of thiophenol, and alcoholic potash breaks it down into potassium thiophenolate and potassium benzene sulphinate (*Fromm*, Ber. 41, 3403). Chlorine brings about fission of the disulphides into two molecules of an aryl-sulphochloride,  $\text{Ar} \cdot \text{S} \cdot \text{Cl}$  (p. 182) (*Zincke*, Ann. 406, 103; cf. free radicals, Vol. IV).

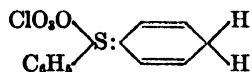
*p,p'*-Diamino-diphenyl disulphide, dithio-aniline,  $\text{S}_2(\text{C}_6\text{H}_4\text{NH}_2)_2$ , m.p. 77°, is obtained together with thio-aniline (see below) when aniline, aniline hydrochloride and sulphur are fused together (*Le Fèvre*, C.r. 198, 1432). On reduction, or on boiling with alcoholic potash it is converted into *p*-aminothiophenol. Its diaceto-compound exists in three forms with m.p. 215°, 182°, and 122°. This isomerism has not yet been explained (*Hinsberg*, Ber. 39, 2427; 41, 626). For dithio-m-tolylene-diamine, see *Schultz*, Ber. 42, 743.

Phenyl sulphide, diphenyl sulphide,  $\text{Ph}_2\text{S}$ , b.p. 292°, d. 1.12, is a colourless liquid with an odour of leaks. It is formed (1) by distilling phenol with phosphorus pentasulphide, thiophenol being also formed. (2) By the action of phosphorus pentasulphide on sodium benzene-sulphonate. (3) By heating mercury diphenyl with sulphur. (4) By heating sulphur with diphenyl sulphone. Phenyl sulphide is re-converted into this sulphone by oxidation (*Kraft*, Ber. 26, 2816; 27, 1771). (5) From benzene with finely divided sulphur or sulphur chloride in the presence of aluminium chloride (*Bösesken*, Rec. 24, 1317; *Hartman*, Ind. Eng. 24, 1317). The last two methods are suitable for preparing phenyl sulphide. It is also obtained (6) by the action of lithium phenyl on diphenyl disulphide (p.



170) (*Schönberg*, Ber. 66, 237, 244), (7) by heating chlorobenzene with aqueous sodium sulphide under pressure (Russ. Pat. 28,219), (8) by heating aromatic lead mercaptides with halogeno-benzenes (the bromobenzenes are best), or sodium mercaptides with iodo-benzenes in the presence of copper powder (*Bourgeois*, Ber. 28, 2322; *Mauthner*, Ber. 39, 3593). This method may be used for the homologues of phenyl sulphide.

*Diphenylene sulphide*, or *dibenzothiophene*, is formed when diphenyl sulphide vapor is passed through a red-hot tube. When solutions of diphenyl sulphide in solvents such as hexane and benzene are treated with chlorine or bromine, highly reactive diphenyl sulphide halides are formed,  $\text{Ph}_2\text{S}(\text{H}X)_2$  (see below, phenyl-methyl sulphide), which react with water to give diphenyl sulfoxide (p. 183). If an excess of halogen is used the *p*-hydrogen in the phenol residue is also substituted (*Fries*, Ann. 381, 337). *Isophenyl sulphide*, *phenyl isosulphide*,  $\text{Ph}_2\text{S}$  (isomerism of a sulphur compound), is a colourless liquid, b.p. 300–340° with partial decomposition, and formation of ordinary phenyl sulphide. *Hinsberg* has prepared it by combining ordinary phenyl sulphide with perchloric acid, when the compound



is formed. This is then boiled with methyl alcoholic potash (Ber. 62, 132; 69, 495). *Iso*-(di-)phenyl sulphoxide is an oil; *iso*-(di-)phenyl sulphone, m.p. 81°.

The *aliphatic-aromatic sulphides*, which may be regarded also as the alcohol ethers of thiophenols, are obtained: (1) from sodium thiophenates by the action of alkyl iodides or dimethyl sulphate (*Brand*, J. pr. 108, 19); (2) by heating phenyl-dithiocarbonic esters alone:  $\text{PhS} \cdot \text{CSOEt} = \text{PhSEt} + \text{COS}$ ; and (3) by the successive action of sulphur and alkyl iodides on phenyl magnesium bromide (*Taboury*, Bull. [3], 35, 668):



*Phenyl-methyl sulphide*, b.p. 187–190°. *o*-Nitrophenyl methyl sulphide, m.p. 64–65°, is obtained from *o,o'*-dinitro-diphenyl disulphide by action of alkaline sodium sulphide, with subsequent methylation (*Brand*, Ber. 54, 1581). *Phenyl-ethyl sulphide*,  $\text{PhSEt}$ , m.p. 200–206°. The aliphatic-aromatic sulphides readily add on 2 atoms of Br or I forming dibromides and diiodides, most of which crystallise easily, and form mixed sulfoxides with water, the halogen atoms being exchanged for oxygen.

The aromatic and aliphatic sulphides combine with dimethyl sulphate to form mixed sulphinium- or sulphonium compounds of which the stability decreases as the number of aromatic radicals in the molecule increases. Thus, diphenyl-methyl-sulphonium chloride decomposes into methyl alcohol and diphenyl sulphide simply on boiling with water, or more rapidly by the action of alkali (*Kehrmann*, Ber. 39, 3559).

Sulphonium chlorides and hydrates of various radicals are obtained from the aluminium chloride compounds of aromatic hydrocarbons with *sym*- or *as*-sulphoxides (*Courtot*, C.r. 197, 1227).

Sulphonium bases of the type  $\text{Ar} \cdot \text{S} \cdot \text{Alk}_2 \cdot \text{OH}$  are obtained in the form of double compounds with mercuric chloride by alkylating the lead compounds of thiophenols (p. 213) with a dialkyl sulphate and then treating them with sodium mercuric chloride,  $\text{NaHgCl}_2$ . *p*-Tolyl-dimethyl-sulphonium hydroxide + mercuric chloride, b.p. 118–120° (*Kehrmann*, Ber. 45, 2895). For purely aromatic sulphonium bases see *Smiles*, J. 89, 696. The methyl-ethyl-phenacyl-sulphonium cation,  $(\text{Me} \cdot \text{Et} \cdot \text{S}^+ \cdot \text{CH}_2\text{COPh})$  has been obtained in an optically active form.

*Phenyl-thioglycollic acid*,  $\text{C}_6\text{H}_5\text{SCH}_2\text{COOH}$ , m.p. 43.5°, is formed (1) by the action of monochloroacetic acid on sodium thiophenate, (2) by the action of thioglycollic acid on phenyl diazonium chloride in aqueous solution. In this action the compound  $\text{C}_6\text{H}_5\text{N}_2\text{S} \cdot \text{CH}_2\text{COOH}$  is formed first, and is converted on warming into phenyl-thioglycollic acid with elimination of nitrogen (*Friedländer*, Mo. 28, 247; Ger. Pats. 194,039/40).

**AMINOPHENYL SULPHIDES, or THIO-ANILINES.** *Methods of formation.*

—(1) By reducing nitrophenyl sulphides (*Kehrmann*, Ber. 29, 2362; *Bourgeois*, Rec. 31, 30). (2) By heating anilines with sulphur and adding lead oxide (*Merz*, Ber. 4, 384). (3) By the action of sulphur chloride on dialkyl-anilines, which produces alkylated *p*-tetra-alkyl-diaminophenyl sulphides. Silver nitrate and ammonia remove the sulphur from the tetra-alkyl compounds, with the formation of *sym*-tetra-alkyl-diaminodiphenyl oxides, *e.g.*,  $O[C_6H_4[4]N(CH_3)_2]_2$  (*Holzmann*, Ber. 21, 2056). On heating the methyl-thio-anilines, *e.g.*, thio-*p*-toluidine, with sulphur to higher temperatures, thiazole derivatives, such as dehydro-thio-toluidine are produced.

*p,p'*-Diamino-diphenyl sulphide, thio-aniline,  $S(C_6H_4NH_2)_2$ , m.p. 105°; *o,o'*-diamino-diphenyl sulphide, m.p. 93° (*Hofmann*, Ber. 27, 2807). For isomeric thioanilines see *Hinsberg*, Ber. 38, 1130. Thio-*p*-toluidine, diamino-ditolyl sulphide,  $S(C_6H_3MeNH_2)_2$ , m.p. 103°.

The sodium salts of thio- and *dithio*-toluidine sulphonic acids dye unmordanted cotton a greenish-yellow; they are so-called substantive dyes (Br. Pat. 6319, 1888). The *bis*-diaz-salts of thio-*p*-toluidine, which may be produced on the fibre itself, combine with naphthylamine sulphonic acids, giving brownish-red bis-azo dyes (*Truhlar*, Ber. 20, 669).

*p*-Thiocyano-aniline,  $NH_2C_6H_4SCN$ , m.p. 57–58°, is prepared from aniline, sodium thiocyanate and bromine in methyl alcoholic or acetic acid solution (*Kaufmann*, Ber. 59, 187; 62, 390).

**THIODIPHENYL-IMIDES.** Thiodiphenylamine,  $\begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} NH$ , is the

simplest of these heterocyclic compounds. *Methylene blue*, a useful dye, is derived from it. The thiophenyl-amino group will be dealt with in the volume on heterocyclic compounds, among the six-membered heterocyclic rings.

**SELENO-PHENOLS.** Selenium, like sulphur, combines with phenyl magnesium bromide and forms  $PhSeMgBr$ , from which seleno-phenol,  $PhSeH$ , b.p. 182°, is obtained by the action of dilute acids. It is also formed by the reduction of benzene seleninic acid, and diphenyl diselenide, into which it is reconverted on exposure to air. Seleno-phenetole,  $PhSeEt$ , b.p. 215–216°, is obtained from phenyl bromide, magnesium, and selenium, the first formed  $PhSeMgBr$  then reacting with ethyl bromide or iodide (*Posner*, Am. 55, 822). *p*-Seleno-cresol, forms white leaflets, m.p. 47° (*Taboury*, Bull. [3], 31, 1183).

**PHENYL SELENIDES and TELLURIDES** are quite readily obtained from mercury-diphenyl compounds by the action of selenium or tellurium. Diphenyl selenide,  $Ph_2Se$ , b.p. 163° (14 mm.), is also recovered as a by-product, in the preparation of phenyl selenocyanide (p. 182), or by heating selenium with diphenyl-sulphone, when sulphur dioxide is liberated. Further action of selenium gives rise to diphenyl diselenide,  $Ph_2Se_2$ , m.p. 63°, b.p. 203° (11 mm.). It is the most stable of the phenyl-selenium compounds, and is also obtained by the action of methyl alcoholic phenol selenocyanide, and, together with seleno-phenol, by the action of selenium on phenyl magnesium bromide (*Behagel*, Ber. 65, 815; *Baroni*, Lincei [6], 11, 579). Diphenyl telluride,  $Ph_2Te$ , b.p. 174° (10 mm.) (*Zeiser*, Ber. 28, 1670; *Kraft*, Ber. 29, 428).

*Selenonium and telluronium compounds.*—Diphenyl selenide gives diphenyl-selenonium dichloride,  $Ph_2SeCl_2$ , m.p. 142° (decomp.) with nascent chlorine, and this gives, with benzene and aluminium chloride, triphenyl-selenonium chloride,  $Ph_3SeCl$ , white crystals, m.p. 230° (decomp.), from which a bromide, m.p. 236° (decomp.) and an iodide, m.p. 237.5° (decomp.) can be obtained. Aqueous alkalis convert the dichloride into diphenyl-selenium oxide,  $Ph_2SeO$ , m.p. 106–108°, and the monohalogen compounds into the base triphenyl-selenonium hydroxide,  $Ph_3SeOH$  (*Leicester*, Am. 51, 3587; *Alquist*, Am. 53, 4033). Diphenyl-telluronium dichloride,  $Ph_2TeCl_2$ , m.p. 160–161°, is obtained by the action of chlorine on diphenyl telluride, or by the action of hydrogen chloride and oxygen upon it. With boiling water it gives the basic hydroxychloride,  $Ph_2Te(OH)Cl$ , m.p. 233–234°. Triphenyl-telluronium iodide, m.p. 247–248°, is obtained by the action of phenyl magnesium iodide on diphenyl-telluronium dichloride (*Lederer*, Ann. 391, 331; Ber. 53, 1430). The optically active phenyl-tolyl-methyl-telluronium ion has been obtained by *Lowry* (J. 1929, 2867).

Other aromatic selenium and tellurium compounds, see *Michaelis*, Ber. 30, 2821; *Lederer*, Ber. 49, 1076; *Behaghel*, C. 1930, II, 1532, *Morgan*, J. 1930, 2599; *Alquist*, Am. 53, 4033; *Leicester*, Am. 53, 4428; *Reichel*, Ann. 523, 201.

*p*-Hydroxyphenyl-telluronium trichloride, forms small yellow plates, m.p. 213°, and is obtained by the action of tellurium tetrachloride on phenol at 90°. It gives an *orychloride* with water, and *p*-hydroxyphenyl-tellyrinic acid, HO[4]-C<sub>6</sub>H<sub>4</sub>[1]TeO<sub>3</sub>H, with sodium hydroxide, both decomposing when warmed (*Reichel*, Ann. 523, 219).

### Dihydric Phenols

Several members of this class either occur in plants or have been obtained as decomposition products of vegetable substances. *Resorcinol*, or *m*-dihydroxybenzene, is of particular importance industrially.

The general methods of formation of the dihydric phenols are analogous to those of the monohydric phenols. They are obtained: (1) from aminophenols, through the diazo-compounds; (2) by fusing (a) monohydric halogeno-phenols, (b) halogeno-benzene sulphonic acids, (c) benzene disulphonic acids, or (d) phenol sulphonic acids, with caustic potash (p. 212); (3) by heating dihydroxybenzene carboxylic acids alone or with lime or baryta; (4) *o*- and *p*-dihydroxyphenols are formed by the reduction of the corresponding quinones; (5) *o*- and *p*-dihydroxybenzenes are formed smoothly when *o*- and *p*-hydroxybenzaldehydes, or *o*- and *p*-hydroxyacetophenones are oxidised with hydrogen peroxide in weakly alkaline solution, but *m*-hydroxybenzaldehyde does not give resorcinol on similar treatment (*Dakin*, Am. Ch. J. 42, 477).

*Reactions*.—The reactions of the dihydroxybenzenes depend on the relative positions of the two hydroxyl groups. Hence the three simple dihydroxybenzenes—catechol, *o*- or (1,2); resorcinol, *m*- or (1,3), and hydroquinone, *p*- or (1,4)—are typical representatives of three groups of dihydric phenols, and will serve as examples to illustrate their reactions. Chlorine converts the dihydric phenols into *hydroaromatic keto-chlorides*, the carbon ring of which is easily ruptured (p. 30). They give dihydroxy-aldehydes with chloroform and alkali, and dihydroxy-carboxylic acids with carbon tetrachloride and alkali, and on heating with aqueous solutions of alkali carbonates. Catechol and hydroquinone can be separated with the aid of C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> (*Mann*, Chem. Ztg. 56, 452). Nascent thiocyanogen acts on catechol, but not on resorcinol or hydroquinone (*Machek*, Mo. 63, 217).

**CATECHOL GROUP.** All the *o*-dihydroxybenzenes give a green coloration with ferric chloride solution. They are distinguished from the *m*- and *p*-compounds by their ability to form cyclic esters by replacement of their hydroxyl hydrogen atoms.

Catechol, *o*-dihydroxybenzene, 1,2-*phendiol*, C<sub>6</sub>H<sub>4</sub>[1,2](OH)<sub>2</sub>, m.p. 104°, b.p. 245°, was first obtained by *Reinsch* in 1839, by dry distillation of *catechin*, the sap of *Mimosa catechu*, and is also obtainable by dry distillation of *Moringa tannic acid*.

Many resins give it when fused with caustic potash. It occurs in *kino*, the dried sap of several species of *Pterocarpus*, *Butea*, and *Eucalyptus*. It is found in coal-tar (*Börnstein*, Ber. 35, 4324), in beech-wood tar, and is a by-product in the

recovery of paraffin from certain bituminous shales. Catechol sulphuric acid occurs in the urine of man, and of the horse.

It is prepared artificially: (1) from phenol, by oxidation with hydrogen peroxide or permonosulphuric acid (*Bamberger*, J. pr. 68, 486); (2) by distilling protocatechuic, or 3,4-dihydroxybenzoic acid; (3) by fusing 1,2-chlorophenol, 1,2-bromophenol, 1,2-benzene disulphonic acid, or 1,2-phenol sulphonie acid with potash; (4) from its mono-methyl ether, guaiacol (see below) by the action of hydrogen iodide at 200°.

On exposure to air its alkaline solution turns green, then blue, and finally black. For the chemistry of this oxidation, see *Weissberger*, Ber. 65, 1815. Lead acetate precipitates white  $C_6H_4O_2Pb$  from an aqueous solution. Neither resorcinol nor hydroquinone shows this reaction. The formation of antimonyl compounds, such as catechol-antimonyl hydroxide,  $C_6H_4O_2SbOH$  (C. 1898, II, 598), is also characteristic of catechol. Catechol reduces silver solutions even in the cold, and alkaline copper solutions on warming. It forms double compounds with its own alkali salts, as well as with those of organic acids (*Weinland*, Ber. 47, 2244). Silver oxide oxidises its solution in ether to *o*-benzoquinone (p. 234). Chlorine converts a solution of catechol in acetic acid into tetrachloro-catechol, tetrachloro-*o*-quinone, and hexachloro-*o*-diketo-cyclohexene (p. 30). Nitrous acid in ether solution oxidises it to dihydroxy tartaric acid. Catechol condenses with a large number of substances with the formation of heterocyclic compounds, the chief of which are shown in the table on p. 221. When heated with phthalic anhydride and sulphuric acid it gives *alizarin* (p. 662) and *hystazarin* (p. 664); cf. protocatechualdehyde and protocatechuic acid. It is used as a developer in photography.

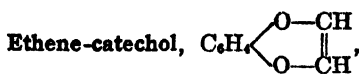
**ETHERS.** Some ethers of catechol, notably the methyl and dimethyl ethers, are of special importance because of their close relationship with many natural vegetable substances, such as eugenol, safrol, apiol, piperonal, papaverin, etc. Catechol methyl ether, guaiacol,  $HO[1]C_6H_4[2]OCH_3$ , m.p. 32°, b.p. 204.7°, is found in the creosote from beech-wood tar (*Béhal*, Bull. [3], 11, 939), and among the distillation products of guaiac resin. It is obtained when catechol is heated with caustic potash and methyl potassium sulphate, or dimethyl sulphate to 180°, by heating calcium vanillate, and from veratrole. (Ger. Pat. 78,310). Its alcoholic solution gives an emerald-green colour with ferric chloride (see vanillin). 5-Chloro-guaiacol,  $Cl[5]C_6H_3[1]OH[2]OCH_3$ , m.p. 37°, is obtained by converting 5-chloro-anisidine into its diazo-compound, and boiling this with copper sulphate solution (Pol. Pat. 9355, 1927). *p*-Nitroso-guaiacol,  $C_6H_3[2,1](OCH_3)(OH)[4]NO$ , obtained from guaiacol, sodium ethylate and ethyl nitrite, gives nitroguaiacol, on oxidation, and amino-guaiacol,  $C_6H_3(OCH_3)(OH)NH_2$ , on reduction (*Rupe*, Ber. 30, 2444). See *Polecoff*, *Robinson*, J. 113, 645, for the nitro-derivatives, and *Rising*, Ber. 39, 3685, and Ger. Pat. 188,506 for the sulphonic derivatives of guaiacol. Numerous derivatives of guaiacol are used in the treatment of pulmonary tuberculosis.

The dimethyl ether, veratrole,  $C_8H_8[1,2](OCH_3)_2$ , m.p. 15°, b.p. 205°, is obtained by the action of methyl iodide or dimethyl sulphate on potassium guaiacolate, or by heating veratric acid with lime. Its dipole moment, and that of the diethyl ether of catechol, indicate an interaction between the alkoxy groups (*Weissberger*, Physikal. Z. 30, 792; cf. p. 227). For bromo-veratrole see *Klemenc*, Mo. 32, 641.

Catechol mono- and di-allyl ethers, b.p. about 82° (4.5 mm.), and 106–107° (5 mm.), respectively, are obtained from catechol, allyl bromide and potassium carbonate in acetone. When heated they rearrange into 3- and 4-allyl-catechols (p. 452) (*Kawai*, Phys. Chem. Japan, 1926).

Catechol methylene- and ethylene-ethers, b.p. 173° and 216°. Glyoxalodicatechol,  $(C_6H_4O_2)CH \cdot CH(C_6H_4O_2)$ , m.p. 89°, obtained from acetylene tetrabromide and sodium catecholate, yields on hydrolysis probably glyoxalo-mono-catechol  $(C_6H_4O_2)CH \cdot CHO$ , as an intermediate, and *o*-hydroxy-phenoxy-acetic acid,  $HOC_6H_4O \cdot CH_2COOH$ , m.p. 131° as final product. The latter is also obtained directly from monosodium catecholate and chloroacetic acid (*Ludwig*, J.

pr. 61, 345; *Carter*, Proc. 16, 152); it readily gives the lactone  $C_6H_4 \begin{array}{c} \diagup O-CH_2 \\ \diagdown O-CO \end{array}$ , m.p. 55°, b.p. 243° (*Bischoff*, Ber. 40, 2779).



*o*-hydroxyphenoxy-acetaldehyde and *o*-hydroxyphenoxy-acetone with acetyl chloride or phosphorus pentoxide (*Moureu*, Ann. ch. ph. [7], 18, 76). Cyclic ethers of the type  $\text{C}_6\text{H}_4:\text{O}_2:\text{CRR}'$  are obtained from catechol by condensation with aldehydes and ketones (*Slooff*, Rec. 54, 995).

Catechol diphenyl ether,  $\text{C}_6\text{H}_4[1,2](\text{OC}_6\text{H}_5)_2$ , m.p.  $93^\circ$ , is obtained by heating *o*-dibromobenzene with potassium phenate in the presence of copper powder. Catechol monophenyl ether,  $\text{OH}[1]\text{C}_6\text{H}_4[2](\text{OC}_6\text{H}_5)$ , m.p.  $107^\circ$ , and *o,o'*-dihydroxyphenyl ether,  $(\text{C}_6\text{H}_4\text{OH})_2\text{O}$ , m.p.  $121^\circ$  are obtained similarly by fusing *o*-bromo-anisole with potassium phenate and guaiacolate, respectively, the mono- and di-methyl ethers being intermediate products. When heated with HBr the

*o,o'*-dihydroxyphenyl ether gives diphenylene dioxide,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{C}_6\text{H}_4$ , m.p.

$119^\circ$  (*Ullmann*, Ber. 39, 622). Mono- and di-benzoyl esters, m.p.  $130^\circ$  and  $84^\circ$ .

Catechol sulphite,  $\text{C}_6\text{H}_4:\text{O}_2:\text{S}:\text{O}$ , b.p.  $211^\circ$  (*Anschütz*, Ber. 27, 752). The following phosphorus derivatives of catechol have been prepared by *Anschütz* and co-workers: Catechyl-phosphorus monochloride, catechol-chlorophosphine,  $\text{C}_6\text{H}_4:\text{O}_2:\text{P}:\text{Cl}$ , m.p.  $30^\circ$  (Ber. 61, 1264). Catechyl-phosphorus trichloride,  $\text{C}_6\text{H}_4:\text{O}_2:\text{P}\text{Cl}_3$ , m.p.  $61\text{--}62^\circ$  (Ann. 454, 109). Catechyl-phosphorus oxychloride,  $\text{C}_6\text{H}_4:\text{O}_2:\text{P}(\text{O})\text{Cl}$ , m.p.  $58\text{--}59^\circ$  (J. pr. 115, 379). Catechyl-phosphorus thiochloride,  $\text{C}_6\text{H}_4:\text{O}_2:\text{P}(\text{S})\text{Cl}$ , m.p.  $49\text{--}50^\circ$  (Ber. 61, 1267). *o*-Phenylene phosphite,  $(\text{C}_6\text{H}_4)_3(\text{PO}_3)_2$ , b.p.  $240\text{--}245^\circ$  (12 mm.) (Ber. 61, 1264). Alkyl- and aryl-*o*-phenylene phosphites,  $\text{C}_6\text{H}_4:\text{O}_2:\text{P}:\text{O}:\text{R}$  (J. pr. 133, 65). *o*-Phenylene phosphate,  $(\text{C}_6\text{H}_4)_3(\text{PO}_4)_2$ , m.p.  $230^\circ$  (J. pr. 115, 380). *o*-Phenylene orthophosphate,  $(\text{C}_6\text{H}_4:\text{O}_2)_3\text{P}_3$ , m.p.  $200\text{--}240^\circ$  (Ann. 454, 116). This compound is an ester of the hypothetical (true) orthophosphoric acid,  $\text{P}(\text{OH})_5$ , and is the first of this class to be discovered. For nomenclature see Ber. 59, 2848, note (1). Aryl-*o*-phenylene thiophosphate,  $\text{C}_6\text{H}_4:\text{O}_2:\text{P}(\text{S})\text{OAr}$  (J. pr. 133, 80). Dicatechyl-phosphorus monochloride,  $\text{C}_6\text{H}_4:\text{O}_2:\text{P}(\text{Cl})\text{O}_2:\text{C}_6\text{H}_4$ , m.p.  $166\text{--}168^\circ$  (Ann. 454, 90, 114).

Catechol carbonate,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{CO}$ , m.p.  $118^\circ$ , b.p.  $227^\circ$ , is obtained from

potassium catecholate by the action of ethyl carbonate or carbonyl chloride, or by the action of phosphorus pentachloride on catechol-methylene ether, and decomposing the resulting catechol-dichloromethylene ether,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{CCl}_2$  with

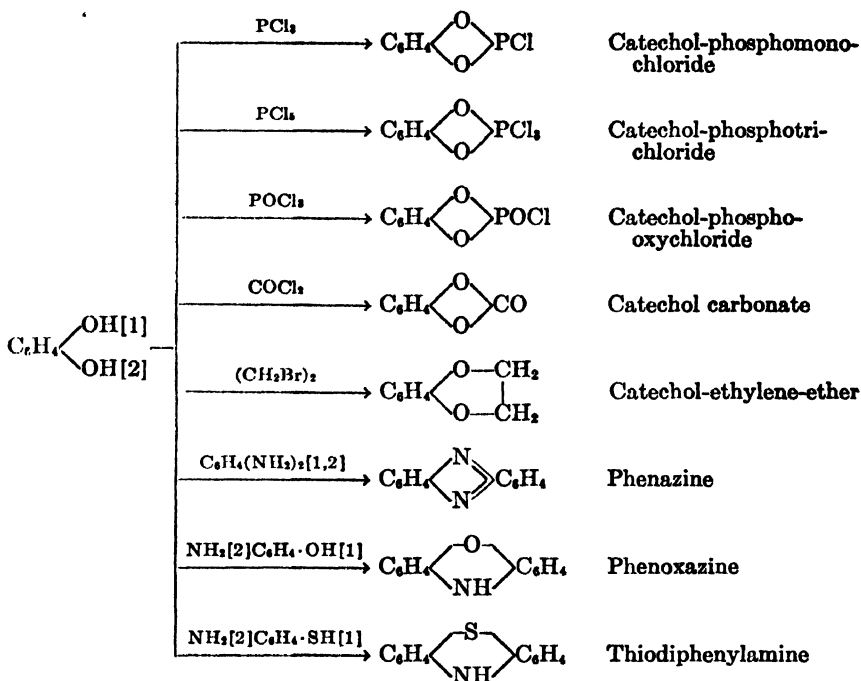
water (*Barger*, J. 93, 563). This reaction is important because it enables numerous natural derivatives of catechol methylene ether to be converted into catechol derivatives, which otherwise might be difficult to obtain; cf. protocatechuic aldehyde.

4-Nitro-catechol, m.p.  $174\text{--}175^\circ$ , is obtained by the nitration of the carbonate, and subsequent hydrolysis, and also from 4-nitro-2-chloro-phenol (Ger. Pat. 264,012; *van Erp*, Ber. 64, 2813). Catechol carbonate is easily broken down when heated with alcohols or amines, *o*-hydroxyphenyl-carbonic esters and carbaminic-*o*-hydroxyphenol esters being formed; with hydrazine hydrate it gives catechol-carbonic hydrazide,  $\text{HOC}_6\text{H}_4\text{OCONHNH}_2$ , which reacts readily with aldehydes in alcoholic solution, but not with ketones (*Wallach*, Ann. 226, 84; *Einhorn*,

Ann. 300, 135; 317, 190). Oxalic ester,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \text{---} \text{CO} \\ \diagdown \text{O} \text{---} \text{CO} \end{array}$ , m.p.  $185^\circ$ , is obtained from sodium catecholate and oxal-ethylic ester acid chloride (*Bischoff*, Ber. 35, 3452).

#### FORMATION OF HETEROCYCLIC COMPOUNDS FROM CATECHOL.

Cyclic esters of catechol are formed when both its hydroxyl hydrogens are replaced by the action of compounds such as thionyl chloride, phosphorus trichloride, phosphorus oxychloride, carbonyl chloride, ethylene dibromide, etc. (see above). *o*-Phenylene diamine, *o*-aminophenol, and *o*-amino-thiophenol condense with catechol to give phenazine, phenoxazine, and thiodiphenylamine.



**HOMOLOGOUS CATECHOLS.** Isohomo-catechol,  $\text{CH}_3[1]\text{C}_6\text{H}_3[2,3](\text{OH})_2$ , m.p.  $45^\circ$ ; 2-methyl ether, crystallising with  $\frac{1}{2}\text{H}_2\text{O}$ , m.p.  $39^\circ$ ; 3-methyl ether, m.p.  $41-42^\circ$ ; dimethyl ether, b.p.  $202-203^\circ$  (*Majima*, Ber. 49, 1482). Homo-catechol,  $\text{CH}_3[1]\text{C}_6\text{H}_3[3,4](\text{OH})_2$ , m.p.  $65^\circ$ , b.p.  $130^\circ$  (11 mm.) (*Anschütz*, Ann. 482, 25) has been prepared from protocatechuic aldehyde by Clemmensen's method. It occurs in beech-wood tar in the form of its 3-methyl ether, creosol,  $\text{CH}_3[1]\text{C}_6\text{H}_3[3](\text{OCH}_3)[4](\text{OH})$ , m.p.  $5.3^\circ$ , b.p.  $221^\circ$ , together with phlorol and guaiacol. Creosol and guaiacol (p. 219) are among the distillation products of guaiac resin. Higher homologues of catechol are obtained by treating it with aliphatic alcohols and zinc chloride (*Tiemann*, Ber. 14, 2005; *Cousin*, Ann. ch. ph. [7], 18, 78; Ger. Pat. 78,882). Homoveratrole, m.p.  $24^\circ$ , has been found in the tar oil from several kinds of wood. 3-Ethoxy-4-hydroxy-1-methyl benzene, m.p.  $34^\circ$ ; 4-ethoxy-3-hydroxy-1-methyl-benzene, m.p.  $58^\circ$  (*Steinkopf*, Ber. 64, 990). 4-Ethyl-2-methoxy-1-hydroxybenzene, ethyl guaiacol, b.p.  $95-96^\circ$  (5 mm.), benzoate, m.p.  $65^\circ$ , phenyl urethane, m.p.  $107^\circ$ , has been detected in the essential oil of camphor and in different wood tar oils (*Rochussen*, J. p. 105, 120). For the synthesis of ethyl guaiacol from vanillin see Ar. Pharm. 268, 312. Dihomocatechyl-phosphorus monochloride,  $\text{CH}_3 \cdot \text{C}_6\text{H}_3 \cdot \text{O}_2 : \text{P}(\text{Cl}) : \text{O}_2 : \text{C}_6\text{H}_3 \cdot \text{CH}_3$ , is an important compound in connection with the problem of the pentavalency of phosphorus (*Anschütz*, Ann. 482, 25). Ethyl-, propyl-, and isopropyl-catechols, melting at  $39^\circ$ ,  $60^\circ$  and  $78^\circ$  respectively, are prepared from the corresponding methylene ethers (*Delange*, C.r. 138, 423, 1701).

4-Propyl-guaiacol, dihydro-eugenol, m.p.  $18-19^\circ$ , is formed when eugenol vapour is catalytically reduced at  $250-270^\circ$  in the presence of copper, and 6-propyl-guaiacol, m.p.  $24^\circ$ , is obtained in a similar way from o-eugenol. Other saturated alkylated catechol ethers have been obtained by hydrogenating methyl-eugenol and safrol. Catechols substituted in the 3- and 4-position by higher alkyl groups have been obtained by the reduction of *uruschiol*, the chief constituent of Japanese lacquer. 3-Pentadecyl-catechol, *hydrouruschiol*, melts at  $58-59^\circ$ . Its dimethyl ether has been synthesised by *Majima* (Ber. 48, 1596) from dimethoxyhydro-caffeyl chloride and the sodium derivative of 1-dodecine.

**Monothio-catechol**,  $C_6H_4[1,2](SH)(OH)$ , m.p.  $5^\circ$ , b.p.  $217^\circ$ , is formed in the reduction of diphenol disulphide,  $(C_6H_4OH)_2S_2$ , obtained by heating sodium phenate with sulphur (*Le Fèvre*, C.r. 198, 1432). The thio-ethers of the former are produced when *o*-amino-thio-ethers are diazotised and the products are boiled with water (*Holt*, Am. 46, 2333). **Dithio-catechol**,  $C_6H_4(SH)_2$ , m.p. about  $28^\circ$ , is obtained by reducing *o*-benzene disulphochloride with tin and hydrochloric acid (*Pollak*, Mo. 34, 1673). *o,o'*-**Dihydroxy-diphenyl sulphide**,  $(C_6H_4OH)_2S$ , m.p.  $142^\circ$  (*Mauthner*, Ber. 39, 1350).

**Diphenylene disulphide**, *thianthrene*,  $C_6H_4 \begin{array}{c} \diagup S \diagdown \\ \diagdown S \diagup \end{array} C_6H_4$ , m.p.  $158^\circ$ , b.p.  $360^\circ$ ,

should be regarded as a derivative of dithio-catechol,  $C_6H_4(SH)_2$ . It is obtained by boiling phenyl sulphide with sulphur; from benzene and sulphur chloride in the presence of aluminium chloride or aluminium amalgam (*Boeseken*, Rec. 24, 209); by heating phenylene diazo-sulphide (p. 215), and by the action of aluminium chloride on thiophenol or phenyl disulphide (*Deuss*, Rec. 28, 136).

When oxidised with nitric acid or chlorine, two forms of *thianthrene disulphoxide*,  $C_6H_4(SO)_2C_6H_4$ , m.p.  $249^\circ$  and  $278^\circ$ , are formed, which have been found to be stereoisomeric, and are of interest in connection with the stereochemistry of sulphur (*Bergmann*, Ber. 65, 457; *Goldschmidt*, "Stereochemie," p. 166). When *thianthrene* is oxidised with chromic acid or permanganate **thianthrene disulphone**,  $C_6H_4(SO_2)_2C_6H_4$ , m.p.  $234^\circ$ , is produced. This, on heating with selenium, gives **diphenylene diselenide**, *selenanthrene*,  $C_6H_4:(Se)_2:C_6H_4$ , m.p.  $181^\circ$ , b.p.  $223^\circ$  (11 mm.) (*Krafft*, Ber. 29, 435, 443).

**Thiocyano-catechol**,  $NCS \cdot C_6H_3(OH)_2$ , m.p.  $142^\circ$ , is obtained from catechol, ammonium thiocyanate, and bromine. Its diacetate melts at  $58^\circ$  (*Machek*, Mo. 63, 218).

**THE RESORCINOL GROUP.** Resorcinol and many of its homologues combine with phthalic anhydride to give *fluoresceins* (p. 548). They give a dark-violet colour with ferric chloride.

**Resorcinol**,  $C_6H_4(1,3)(OH)_2$ , m.p.  $111^\circ$ , b.p.  $276^\circ$ , is obtained from *galbanum*, *asafoetida*, and other resins on heating with potash, and by distilling Brazil-wood extract. Many *m*-disubstitution products of benzene give rise to it when fused with potash or soda at  $230$ – $280^\circ$ . A few examples are 1,3-chloro- and 1,3-iodo-phenol, 1,3-phenol sulphonic acid, 1,3-benzene disulphonic acid, etc. *Umbelliferone* also gives it under similar circumstances. Even *o*- and *p*-compounds give resorcinol on fusion with potash or soda, especially at higher temperatures. Hence fusion with potash cannot be used for determination of constitution (p. 197). Resorcinol is obtained industrially from *m*-benzene disulphonic acid (*Degener*, J. pr. 20, 318).

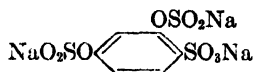
**Properties and reactions.**—Resorcinol crystallises in rhombic prisms or plates. It dissolves readily in water, alcohol, and ether, but not in chloroform or carbon disulphide. It has an intensely sweet taste. Its aqueous solution gives no precipitate with lead acetate, and may thus be distinguished from catechol.

Sodium amalgam converts resorcinol into dihydro-resorcinol (Ann. 278, 20), or *m*-cyclohexane-dione (Vol. II, p. 111). Bromine water gives tribromo-resorcinol, m.p.  $111^\circ$ . Chlorine in acetic acid ultimately converts it into heptachloro-resorcinol (p. 31), the ring of which is easily opened (*Zincke*, Ber. 26, 498). When fused with soda it is converted into phloroglucinol, catechol, and diresorcinol  $(HO)_2C_6H_2 \cdot C_6H_3(OH)_2$  (Ber. 26, R 233). On heating with HCl the hydrochloride of a triresorcinol,  $C_{12}H_{14}O_4$ , is obtained. For the action of acetylene on resorcinol, see Flood, Am. 45, 1536.

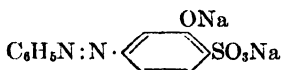
**ETHERS AND ESTERS OF RESORCINOL.** Monomethyl ether, b.p.  $243^\circ$  (*Dey*, Indian J. 12, 685); dimethyl ether, b.p.  $214^\circ$  (*Habermann*, Ber. 10, 868), dipole moment 1.7–1.75 D.; diphenyl ether, b.p.  $61^\circ$  (*Fullmann*, Ann. 350, 96;

diacetyl ester, b.p. 278° (*Typke*, Ber. 16, 552); dicarbonic ester,  $C_6H_4(OCOOC_2H_5)_2$ , b.p. 300° (*Bender*, Ber. 13, 697); dibenzoic ester, b.p. 117° (*Dobner*, Ann. 210, 256); diethyl ether has dipole moment 1.7 D.

Resorcinol combines with various sugars in the presence of HCl (*Fischer*, Ber. 27, 1356). When heated with phthalic anhydride, resorcinol gives *fluorescein*. With sodium nitrite, a deep-blue dye is formed, which turns red with acids. This is the indicator *lacmoid* (*Traub*, Ber. 17, 2617; 18, R 126). Nitric acid containing nitrous acid gives the dyes *resorufin* and *resazurin*, which are derivatives of phenoxazine (*Nietzki*, Ber. 23, 718). Resorcinol combines with three molecules of sodium bisulphite to form a di-ester sulphonate



which gives the *m*-hydroxy-azo dye



with phenylhydrazine (*Bucherer*, J. pr. 121, 113). Buff-coloured azo-dyes are formed from resorcinol and sodium nitrite, formic acid and sulphuric acid, and from resorcinol and diazotised nitrilines.

When phenyl-diazonium nitrate or chloride acts upon aqueous or alkaline solutions of resorcinol, the products are: **benzene-azo-resorcinol**,  $(PhN_2)C_6H_3(OH)_2$  (for its constitution see *Orndorff*, Am. Ch. J. 26, 159),  $\alpha$ - and  $\beta$ -**resorcinol-bis-azobenzene**  $(PhN_2)_2C_6H_2(OH)_2$  (*Wallach*, Ber. 15, 2816; *Liebermann*, Ber. 16, 2858; 17, 880) and **resorcinol-tris-azobenzene**,  $(PhN_2)_3C_6H(OH)_2$  m.p. 254° (*Orndorff*, Ber. 40, 3211).

By the action of amyl nitrite on an alkaline solution of resorcinol, **4-nitroso-resorcinol**,  $NO[4]C_6H_3[1,3](OH)_2$ , is formed (*Henrich*, Ber. 35, 4191), while in acid solution, **dinitroso-resorcinol**, or **diquinoyl-dioxime**,  $C_6H_3[1,3](OH)_2[2,4](NO)_2$ , or  $C_6H_2O_2(NO)_2$ , is immediately formed as yellowish-brown leaflets which deflagrate at 115°. This substance is put on the market as the dye *solid green*, or *chlorin*. The same compound is obtained by the action of  $NaNO_2$  and glacial acetic acid and, like  $\alpha$ -nitroso- $\beta$ -naphthol, is used for the detection of cobalt (*Orndorff*, *Nichols*, Am. 45, 1536). **1-Methoxy- and 1-ethoxy-3-hydroxy-4-nitrosobenzene**,  $NO[4]C_6H_3[3](OH)[1]OCH_3$  and  $OC_2H_5$ , exist in two isomeric modifications, a labile green form and a stable yellow-brown form. When heated to 130°, the former is transformed into the latter. Both modifications yield the same alkali salts, from whose solutions the yellow-brown modification is precipitated by acid. The isomerism may be of this type:  $(RO)C_6H_3(OH)NO$  and  $(RO)C_6H_3O:(NOH)$ , the green form being the true nitroso compound and the yellow-brown form, the quinone-oxime (J. pr. 70, 332; see p. 202).

***v*-Nitroresorcinol**,  $(NO_2)[2]C_6H_3[1,3](OH)_2$ , orange-red needles, volatile with steam, results from the nitration of resorcinol-disulphonic acid and subsequent removal of the sulphonic acid groups by superheated steam (*Kauffmann*, Ber. 37, 726).

***v*-Dinitroresorcinol**,  $(NO_2)[2,4]C_6H_2[1,3](OH)_2$ , m.p. 148°, is formed by treatment of resorcinol with nitric acid vapours and by boiling dinitroresoreylic acid with water (*Hemmelmayer*, Mo. 26, 185). **4,6-Dinitroresorcinol**,  $(NO_2)_2[4,6]C_6H_3[1,3](OH)_2$ , m.p. 212°.

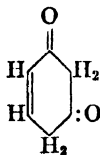
**2,4,6-Trinitroresorcinol**, **styphnic acid**, **hydroxypticric acid**,  $(NO_2)_3[2,4,6]C_6H[1,3](OH)_2$ , m.p. 175°, is obtained by the action of cold nitric acid on resorcinol or resorcinol disulphonic acid and various gum resins, such as *galbanum*, and also by nitration of *m*-nitrophenol and several dinitrophenols. With hydrous ferrous sulphate and lime water it gives a green colouration (picric acid: blood red). The diethyl ether, m.p. 120° (*Pollak*, C. 1903, II, 829), is reduced by tin and hydrochloric acid to the **tri-amino-resorcinol ether**. Like picric acid, styphnic acid forms crystalline molecular compounds with hydrocarbons such as naphthalene and phenanthrene and with amines (*Gibson*, Proc. Chem. Soc. 24, 241; *Jefremov*, J. Russ. Phys. Chem. Soc. 51, 353). Oxidation with bromine at ordinary temperatures converts styphnic acid to hexabromo-trinitro-iso-valeric acid,  $\{(NO_2)_3-$



$\text{Br}_2\text{C}$ ):  $\text{CBr}\cdot\text{C}[\text{NO}_2]\text{BrCOOH}$ , m.p.  $116\text{--}117^\circ$  (Wieland, Jung, Ann. 445, 82).

Tetranitro-resorcinol,  $(\text{NO}_2)_4\text{C}_6(\text{OH})_2$ , m.p.  $152^\circ$ , is converted by boiling water to trinitro-phloroglucinol (Blanksma, Rec. 27, 25).

Monothio-resorcinol,  $\text{C}_6\text{H}_4[1]\text{OH}[3]\text{SH}$ , b.p.  $168^\circ$  (35 mm.), is prepared from sodium 1,3-phenol sulphonate through the carboxy-compound, the sulphochloride, and the mercaptan, which is saponified (Zincke, Ebel, Ber. 47, 923). Dithio-resorcinol, *thio-resorcinol*,  $\text{C}_6\text{H}_4[1,3](\text{SH})_2$ , m.p.  $25^\circ$ , b.p.  $243^\circ$ , the reduction product of *m*-benzene disulphonyl chloride, is converted by heating with phenyl isocyanate to a bis-phenylcarbamate,  $\text{C}_6\text{H}_4(\text{SCONHC}_6\text{H}_5)_2$ , m.p.  $179^\circ$  (Bourgeois, Rec. 18, 426; Snape, J. 69, 98). Dibenzyl-thioresorcinol,  $\text{C}_6\text{H}_4(\text{SCH}_2\text{C}_6\text{H}_5)_2$ , m.p.  $60^\circ$ , is prepared from dithio-resorcinol, benzyl chloride, and sodium hydroxide (Finzi, Gazz. 44, I, 598). Resorcinol combines with sodium bisulphite at  $100^\circ$  to form the bisulphite compound of a 3,5-diketocyclohexene-sulphonic acid derived from the tautomeric quinone form of resorcinol (Fuchs, Ber. 53, 886; cf. Bucherer, Ber. 53, 1457; Herzig, Ber. 53, 1518):



**HOMOLOGOUS RESORCINOLS.** Alkylated resorcinols are produced by reducing acyl-resorcinols (themselves readily obtained from resorcinol and fatty acids in the presence of zinc chloride) with amalgamated zinc and hydrochloric acid. Like resorcinol itself, they are used as antiseptics (Br. Pats. 219,922, 222,136, 224,913, and 250,892). Orcinol, more fully treated below, is by far the most important of the homologous resorcinols, of which the formulae and melting points are given in the table below:

| Resorcinol                                                                                             | M.p.                    | B.p.        | Reference                   |
|--------------------------------------------------------------------------------------------------------|-------------------------|-------------|-----------------------------|
| Orcinol, $\text{CH}_3[1]\text{C}_6\text{H}_3[3,5](\text{OH})_2$ .....                                  | $107^\circ$             | $290^\circ$ |                             |
| Cresorcinol, $\text{CH}_3[1]\text{C}_6\text{H}_4[2,4](\text{OH})_2$ ...                                | $104^\circ$             | $269^\circ$ | (Noelting, Ber. 19, 136)    |
| 2,5-Dihydroxytoluene,<br>$\text{CH}_3[1]\text{C}_6\text{H}_3[2,5](\text{OH})_2$ .....                  | $128^\circ$             | ..          | (Nietzki, Ann. 215, 159)    |
| 2,6-Dihydroxytoluene,<br>$\text{CH}_3[1]\text{C}_6\text{H}_3[2,6](\text{OH})_2$ .....                  | $116\text{--}121^\circ$ | ..          | (Herzig, Mo. 24, 906)       |
| 3,5-Dihydroxy- <i>o</i> -xylene,<br>$(\text{CH}_3)_2[1,2]\text{C}_6\text{H}_3[3,5](\text{OH})_2$ ..... | $137^\circ$             | ..          | (Simon, Ann. 329, 305)      |
| 2,4-Dihydroxy- <i>m</i> -xylene,<br>$(\text{CH}_3)_2[1,3]\text{C}_6\text{H}_3[2,4](\text{OH})_2$ ..... | $148^\circ$             | ..          | (Ber. 23 3119)              |
| <i>m</i> -Xylorcinol,<br>$(\text{CH}_3)_2[1,3]\text{C}_6\text{H}_3[4,6](\text{OH})_2$ .....            | $125^\circ$             | $277^\circ$ | (Kostanecki, Ber. 19, 2315) |
| $\beta$ -Orcinol, $(\text{CH}_3)_2[1,4]\text{C}_6\text{H}_3[3,5](\text{OH})_2$ .                       | $149^\circ$             | $275^\circ$ | (Knecht, Ann. 215, 100)     |
| Mesorcinol,<br>$(\text{CH}_3)_2[1,3,5]\text{C}_6\text{H}_2[2,4](\text{OH})_2$ .....                    | $163^\circ$             | $279^\circ$ | (Sonn, Ber., 49, 621)       |
| <i>n</i> -Propylresorcinol,<br>$\text{C}_3\text{H}_7[1]\text{C}_6\text{H}_3[2,4](\text{OH})_2$ .....   | $107\text{--}108^\circ$ | ..          | (Johnson, Ann. 35, 1014)    |
| Di-tert.-amylresorcinol,<br>$(\text{C}_4\text{H}_9)_2\text{C}_6\text{H}_3[1,3](\text{OH})_2$ .....     | $89^\circ$              | ..          | (Gurswitsch, Ber. 25, 2653) |
| Di-tert.-amylresorcinol,<br>$(\text{C}_4\text{H}_9)_2\text{C}_6\text{H}_3[1,3](\text{OH})_2$ .....     | $67^\circ$              | ..          | (Ber. 32, 2426)             |

Orcinol, 3,5-dihydroxy-toluene,  $\text{CH}_3(1)\text{C}_6\text{H}_3[3,5](\text{OH})_2$ , (Neville, Ber. 15, 2995), occurs in many lichens of the species *Roccella*, and *Lecanora*, partly as *orcinol-carboxylic acid* (orsellinic acid), and partly

as *erythrin* (diorsellinic erythritol ester) (Vol. I, p. 649). It is prepared from orsellinic acid by fusion, or by boiling with water, alcohol, lime water or baryta water, and is also obtained by fusing the extract of aloes with caustic potash.

It has been obtained from 1,3,5-dinitrotoluene and other toluene derivatives (Ber. 15, 2992); by the distillation of silver dihydroxyphenyl-acetate,  $(\text{HO})_2\text{C}_6\text{H}_3[\text{CH}_2\text{COOAg}]$ ; and by heating dehydracetic acid (Vol. I, p. 626) with concentrated caustic soda (Collie, J. 63, 122). For its synthesis from 1-methyl-cyclobutane-2-one-1-yl-acetic ester see Ingold, J. 121, 1143.

Orcinol crystallises with 1  $\text{H}_2\text{O}$  in colourless, hexagonal prisms. It dissolves freely in water, alcohol, and ether, and has a sweet taste. The hydrate melts at about  $56^\circ$ , gradually loses water and melts in the anhydrous state at  $107^\circ$ ; b.p.  $290^\circ$ . For the existence of two modifications see Schaum, Ann. 411, 193. Lead acetate precipitates its aqueous solutions, and with ferric chloride, orcinol gives a bluish-violet colour. With bleaching powder a fugitive dark-violet colour is produced. Diazo-compounds form azo-dyes. Phthalic anhydride does not give a fluorescein (p. 223). When treated with chlorine in acetic acid it gives trichloro-orcinol, m.p.  $127^\circ$ , and with chlorine in chloroform pentachloro-orcinol, or 1,3,5-diketo-methyl-2,2,4,4,6,6-pentachloro- $\Delta^4$ -cyclohexene, m.p.  $120^\circ$  (Zincke, Ber. 26, 317).

Dinitroso-orcinol,  $\text{CH}_3 \cdot \text{C}_6\text{H}(\text{OH})_2(\text{NO})_2$ , see Goldschmidt, Ber. 20, 1608. Nitroso-orcinol, *hydroxy-tolu-o-quinone-oxime*,  $\text{CH}_3[1]\text{C}_6\text{H}_2[3,5,4](\text{OH})_2(\text{NO})$ , exists in two modifications—dark-red needles and bright yellow crystals. The first change to the second when heated to  $128^\circ$  (Hantzsch, Ber. 39, 162). It must be regarded as a derivative of an *o*-quinone because its methyl ether, obtained by methylating the quinone-oxime as well as from orcinol monomethyl ether, m.p.  $63^\circ$ , with nitrogen trioxide, gives an aminophenol on reduction (Henrich, Ber. 32, 3419; 36, 882). For amino-orcinol and its oxidation products, which are related to the naturally occurring *litmus* (see below), see Henrich, Mo. 19, 483; C. 1903, I, 25).

When an ammoniacal solution of orcinol is allowed to stand in air, *orcein*,  $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_7$ , separates out as a fawn-coloured amorphous powder (Zulkowski, Mo. 11, 227; Herzig, Mo. 24, 885). It dissolves in alcohol and in alkalis giving a dark-red solution and is precipitated from these solutions by the addition of acids. It gives red mordant dyes with metallic salts. Orcein is the chief constituent of commercial *orseille* (also known as persio, cudbear, and French purple), which is extracted from the same lichens as orcinol by treatment with ammonia and air. *Litmus* is made from the lichens *Rocella* and *Lecanora* by the action of ammonia and potassium carbonate. The concentrated solution of the blue potassium salt formed is mixed with chalk or gypsum and is the commercial litmus.

*iso*-Orcinol, *cresorcinol*, or  $\gamma$ -*orcinol* is obtained from 2,4-toluene disulphonic acid by fusion with potash, from amino-*o*-cresol, *etc.*, and also from methylene *bis*-resorcinol (p. 512), the reaction product of formaldehyde and resorcinol, by reduction with zinc dust and caustic soda. By repeating the condensation with formaldehyde and reducing the resulting methylene-*bis*-cresorcinol, *m*-xylorcinol is obtained (Luther, Arch. Ph. 244, 561). 3,5-Dihydroxy-*o*-xylene and 1,2,6-trimethyl-3,5-dihydroxy-benzene are similarly obtained from orcinol (Simon, Ann. 329, 305). *p*-Xylorcinol, or  $\beta$ -*orcinol*, is obtained from *m*-dinitro-*p*-xylene, and has been isolated from the distillation products of various lichen acids, *e.g.*, usnic acid. It rapidly turns red in air containing ammonia. *Mesorcinol*, or *dihydroxy-mesitylene* is obtained from dinitro-mesitylene.

*n*-Propyl-3,5-dihydroxybenzene, *divarin*, m.p.  $44^\circ$  (hydrated), occurs in the lichen *Evernia divaricata*, and has been artificially prepared from methyl ethers of *n*-propyl-pyrogallol (*q.v.*) found in beech-wood tar, by exhaustive methylation, removal of the *p*-methoxy-group, and hydrolysis of the remaining methoxy-groups

(Sonn, Ber. 57, 959). *n*-Amyl-3,5-dihydroxybenzene, *olivitol*, m.p. 40–41°, is a decomposition product of the Japanese lichen *Alectoria divergens*, and has been synthesised from *n*-caproyl-acetic ester and acetone-dicarboxylic ester with sodium (Asahina, Ber. 65, 479).

**THE HYDROQUINONE GROUP.** The *p*-dihydroxy-benzenes are usually called hydroquinones, because they are readily formed by the reduction of *p*-quinones, and are just as readily converted into quinones by oxidation with ferric chloride. The more rational name suggested, "quinols," is, unfortunately, used for another group of substances (p. 340).

**Hydroquinone**, *p*-dihydroxy-benzene,  $C_6H_4[1,4](OH)_2$ , m.p. 169°, was discovered by Wöhler (Ann. 65, 349), among the distillation products of quinic acid. It can be obtained by heating an aqueous solution of quinic acid with lead dioxide:



It is formed, together with glucose, by the hydrolysis of the glucoside *arbutin* (Vol. II, p. 355), and occurs in *Protea mellifera* (Ber. 29, R 416). It is also obtained by the electrolytic oxidation of an alcoholic solution of benzene containing sulphuric acid (Gattermann, Ber. 27, 1942), by heating *p*-halogeno-phenols with aqueous caustic alkali at 180°, from 5-hydroxy-salicylic acid, from *p*-aminophenol, and, in small quantities, by the distillation of succinates.

In the preparation of hydroquinone, quinone is reduced by sulphur dioxide, the aqueous solution is extracted with ether, and the substance is recrystallised from hot water containing a little sulphur dioxide. The solution is purified by the addition of animal charcoal (Nietzki, Ber. 19, 1467). U. S. Pat. 1,849,844 describes its manufacture by the hydrolysis of *p*-dichloro-benzene in an autoclave. Tolu-hydroquinone has been prepared by the action of hydrogen peroxide on *o*-cresol in the presence of ferrous sulphate (Ono, Bull. Japan 11, 132).

Hydroquinone is dimorphous. It sublimes in monoclinic leaflets, and crystallises in hexagonal prisms. It decomposes on rapid heating. It dissolves freely in water, alcohol, and ether. It forms crystalline compounds with hydrogen sulphide and sulphur dioxide, which are decomposed by water. Its solutions give a reddish-brown colour with ammonia. Oxidising agents, such as ferric chloride, potassium dichromate and sulphuric acid, convert it into quinone, with the intermediate formation of *quinhydrone*. It reacts with oxygen in alkaline solution, with the formation of highly coloured crystalline substances which have not yet been fully investigated (Harger, Proc. Wash. 3, 57; Euler, Z. physikal. Chem. 139, 615). Hydroquinone is oxidised by Fehling's solution to dihydroxy-quinone (p. 239) (Pinnow, J. pr. 98, 81). Like quinone, it forms *quinone-dioxime* with hydroxylamine (p. 241) (Renaut, Ber. 22, 1283). It does not couple with diazonium salts to give azo-compounds, but is, instead, oxidised to quinone (Orton, J. 93, 1010).

Hydroquinone is used as a developer in photography, as an inhibitor in cases of autoxidation, and as an antifermentative and antipyretic.

**Ethers:** Hydroquinone monomethyl ether,  $MeO[4]C_6H_4[1]OH$ , m.p. 56°, b.p. 247°, has been obtained from *methyl-arbutin* (Vol. II, p. 355) and by the action of methyl iodide and caustic potash on hydroquinone. The methylation can also be effected with potassium methyl sulphate or dimethyl sulphate (Tiemann, Ber. 14, 1989; J. 1926, 304). Dimethyl ether, m.p. 56.8°, b.p. 205°. Ethyl ether, m.p. 66°, b.p. 246°, occurs in small quantities in star anise oil. Diethyl ether, m.p. 71°. Diphenyl ether, m.p. 77° (Ullmann, Ann. 350, 97).

The *dipole moments* of hydroquinone dimethyl and diethyl ethers have been found to be approximately 1 D., which shows that the two

valencies of each oxygen atom do not form a straight line, as, if this were the case, the dipole moment would be zero. It can be deduced that the angle formed by these valencies is not far from  $109^\circ$ , the tetrahedral angle of the carbon valencies, and also that the  $\text{—O—R}$  groups, at the temperature of the determination ( $25^\circ$ ) rotate freely about the phenyl-oxygen link. Their mutual electrostatic induction is negligible compared with their kinetic energy (*Weissberger*, *Phys. Z.* **30**, 792). For the relationship between dipole moment and structure see *Hückel*, *Theoretische Grundlagen*, II, 36 *et seq.*, 49.

**Hydroquinone-bis-chloro-phosphine**,  $\text{C}_6\text{H}_4(\text{OPCl}_2)_2$ , m.p.  $65^\circ$ , b.p.  $200^\circ$  (65 mm.). **Hydroquinone-bis-oxychloro-phosphine**,  $\text{C}_6\text{H}_4(\text{OPOCl}_2)_2$ , m.p.  $123^\circ$ , b.p.  $270^\circ$  (70 mm.) (*Knauer*, *Ber.* **27**, 2568). **Hydroquinone diacetate**,  $\text{C}_6\text{H}_4(\text{OCOCH}_3)_2$ , m.p.  $123^\circ$ . **Hydroquinone dibenzoate**,  $\text{C}_6\text{H}_4(\text{OCOPh})_2$ , m.p.  $199^\circ$ .

**HOMOLOGOUS HYDROQUINONES.** These are usually prepared by the action of sulphur dioxide on the homologues of the quinones. **Tolu-hydroquinone** and some other homologues are also obtained from *p*-tolyl-hydroxylamine and other *p*-alkyl-phenyl-hydroxylamines by the action of hot dilute sulphuric acid. The mechanism appears to be that *quinols* (p. 340) are first formed, and then rearrange. The formation of tolu-hydroquinone by the oxidation of *p*-cresol with Caro's acid, a rather unexpected reaction, is also due to the intermediate formation of toluquinol (*Kunagai*, *Ber.* **41**, 299). Alkaline permanganate normally produces homocatechol. **Hydro-*p*-xyloquinone** is called *hydrophlorone*. **Dimethyl-hydrothymoquinone**, b.p.  $249^\circ$ , is found in the essential oil of *Arnica montana* (*Ann.* **170**, 363) and in ayapana oil from *Eupatorium Ayapana* (*Ber.* **41**, 509). **Di-tert.-amyl-hydroquinone** is formed from hydroquinone and iso-amylene by the action of acetic acid and sulphuric acid (*Königs*, *Ber.* **25**, 2650).

**Toluhydroquinone**,  $\text{CH}_3[1]\text{C}_6\text{H}_3[2,5](\text{OH})_2$ , m.p.  $124^\circ$  (*Nietzki*, *Ann.* **215**, 159; *Neirille*, *Ber.* **15**, 2981).

***o*-Xylohydroquinone**,  $(\text{CH}_3)_2[1,2]\text{C}_6\text{H}_2[3,6](\text{OH})_2$ , m.p.  $221^\circ$  (*Klingel*, *Ber.* **18**, 2673).

***m*-Xylohydroquinone**,  $(\text{CH}_3)_2[1,3]\text{C}_6\text{H}_2[2,5](\text{OH})_2$ , m.p.  $150^\circ$  (*Noelting*, *Ber.* **18**, 1151).

***p*-Xylohydroquinone**,  $(\text{CH}_3)_2[1,4]\text{C}_6\text{H}_2[2,5](\text{OH})_2$ , m.p.  $213^\circ$  (*Sabatier*, *C.r.* **146**, 458).

**Pseudocumohydroquinone**,  $(\text{CH}_3)_3[1,2,4]\text{C}_6\text{H}[2,5](\text{OH})_2$ , m.p.  $169^\circ$  (*Noelting*, *Ber.* **18**, 1152).

**Thymohydroquinone**,  $(\text{CH}_3)(\text{C}_2\text{H}_7)[1,4]\text{C}_6\text{H}_2[2,5](\text{OH})_2$ , m.p.  $139^\circ$ ; b.p.  $290^\circ$ .

**Di-tert.-amylhydroquinone**,  $(\text{C}_4\text{H}_{11})_2\text{C}_6\text{H}_2[1,4](\text{OH})_2$ , m.p.  $185^\circ$ .

**SUBSTITUTED HYDROQUINONES.** Monochloro- and monobromo-hydroquinones have been obtained by the action of concentrated hydrochloric and hydrobromic acids, respectively, on *p*-quinone (*Wickelhaus*, *Ber.* **12**, 1504; *Levy*, *Ann.* **210**, 153), and dichloro-hydroquinone has been obtained similarly from monochloro-quinone, *etc.* Di-, tri-, and tetra-chloro-hydroquinones are obtained by the action of sulphur dioxide on the corresponding chloro-quinones. Tetrachloro-hydroquinone forms esters with fatty acids which crystallise readily (*Bouvaull*, *C.r.* **129**, 53).

**Monochloro-hydroquinone**, m.p.  $104^\circ$

**2,5-Dichloro-hydroquinone**, m.p.  $172^\circ$

**2,6-Dichloro-hydroquinone**, m.p.  $165^\circ$

**Trichloro-hydroquinone**, m.p.  $134^\circ$

**Tetrachloro-hydroquinone**, m.p.  $232^\circ$

**Monobromo-hydroquinone**, m.p.  $116^\circ$

**2,5-Dibromo-hydroquinone**, m.p.  $186^\circ$

**2,6-Dibromo-hydroquinone**, m.p.  $163^\circ$

**Tribromo-hydroquinone**, m.p.  $136^\circ$

**Tetrabromo-hydroquinone**, m.p.  $244^\circ$

**Nitro-hydroquinone**, m.p.  $193^\circ$ , is obtained by the action of ammonium persulphate on nitrophenol (*Elbs*, *J. pr.* **48**, 179). **2,3- and 2,5-Dinitro-diethyl-**

hydroquinone, m.p. 130° and 176° (*Nietzki*, Ann. 215, 149) are obtained by nitration of hydroquinone diethyl ether, and give the same trinitro-diethyl-hydroquinone, m.p. 130°. 2,5-Dinitro-hydroquinone diacetate, m.p. 96°, obtained by nitration of hydroquinone diacetate, readily exchanges one NO<sub>2</sub> group for NHPh. 2,6-Dinitro-hydroquinone, m.p. 135°, is obtained from 2,6-dinitro-arbutin, or from dinitro-hydroquinone diacetate. On reduction of the nitro-compounds, amino-hydroquinones are formed (*Nietzki*, Ber. 24, 3824; *Richter*, Ber. 49, 1398). 1,4-Diamino-hydroquinone is obtained from 2,5-dihydroxy-quinone dioxime (p. 239). Triazo-hydroquinone, C<sub>6</sub>H<sub>3</sub>[1,4](OH)<sub>2</sub>[3]N<sub>3</sub>, forms white explosive leaflets, and is formed by the action of excess of hydrazoic acid in benzene solution on quinone. It dissolves in dilute solutions of caustic alkalis with decomposition (*Oliveri*, Gazz. 45, I, 307; II, 138).

Dichloro-hydroquinone-disulphonic acid, (HO)<sub>2</sub>C<sub>6</sub>Cl<sub>2</sub>(SO<sub>3</sub>H)<sub>2</sub>, is obtained by the action of potassium bisulphite on tetrachloro-quinone (*Hesse*, Ann. 114, 324). Its aqueous solution gives an indigo-blue colour with ferric chloride. When boiled with caustic potash it gives *euthiochronic acid* (p. 240), taking up oxygen from the air.

Monothio-hydroquinone, C<sub>6</sub>H<sub>4</sub>[1,4](OH)(SH), m.p. 30°, b.p. 167° (45 mm.), can be prepared by the action of potassium xanthate on *p*-diazophenol chloride, or from sodium-1-carbethoxyphenol-4-sulphonate by first converting it into a chloride, then reducing this to carbethoxy-mercaptan, and finally hydrolysing the latter (*Zincke*, Ber. 47, 1100). *p*-Hydroxy-diphenyl sulphide, PhS[1]C<sub>6</sub>H<sub>4</sub>-[4]OH, m.p. 25°, is obtained by heating phenol with benzene sulphonic acid to 150° (Ger. Pats. 147,552, 147,580, and 147,634). *p,p'*-Dimethoxy-diphenyl sulphide, *diamisyl sulphide*, S(C<sub>6</sub>H<sub>4</sub>OMe)<sub>2</sub>, m.p. 46°, and similar compounds are produced, together with sulfoxides and sulphonium salts, when thionyl chloride or sulphur monochloride, and aluminium chloride act upon phenol ethers (*Loth*, Ber. 27, 2540; *Smiles*, J. 93, 745).

Dithio-hydroquinone, C<sub>6</sub>H<sub>4</sub>[1,4](SH)<sub>2</sub>, m.p. 98°, is obtained from *p*-benzene disulphonic chloride, or from *p*-diazophenyl disulphide. It is gradually oxidised by atmospheric oxygen to *p*-phenylene disulphide (C<sub>6</sub>H<sub>4</sub>S<sub>2</sub>)<sub>2</sub>. When methylated it gives *p*-phenylene dimethyl-disulphide, C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>, m.p. 85°, and this, on oxidation with nitric acid, gives a disulphoxide, C<sub>6</sub>H<sub>4</sub>(SOMe)<sub>2</sub>, m.p. 188°, and a disulphone, C<sub>6</sub>H<sub>4</sub>(SO<sub>2</sub>Me)<sub>2</sub>, m.p. 260° (*Zincke*, Ber. 42, 2721). The tetrabromide of dithiohydroquinone dimethyl ether exists in two forms with m.p. 67–70° and 107–109° thought to be stereoisomeric. Dihydroxy-disulphides, HO·C<sub>6</sub>H<sub>4</sub>S·S·C<sub>6</sub>H<sub>4</sub>·OH, are obtained by the action of sulphur on phenols (*Le Fèvre*, C.r. 198, 432). Dibenzyl-thio-hydroquinone, C<sub>6</sub>H<sub>4</sub>[1,4](SCH<sub>2</sub>Ph)<sub>2</sub>, m.p. 127°, is obtained by the action of benzyl chloride and sodium hydroxide on dithiohydroquinone (*Finzi*, Gazz. 44, I, 593).

***p*-THIOCYANO-PHENOLS, PHENOL THIOCYANATES**, and their alkyl ethers are obtained by treating phenols and phenol ethers with a methyl alcoholic solution of sodium thiocyanate and then brominating, or by acting upon diazotised anisidine or phenetidine with cuprous thiocyanate. In the latter reaction, isothiocyanates or "alkoxyphenyl-mustard oils" (p. 207) are also formed as by-products. The isothiocyanates give thio-urea derivatives (Vol. I, p. 508) when treated with ammonia, while the thiocyanates themselves do not. The mustard oils are not produced by a thermal rearrangement of thiocyanates, which are not affected by heat. 4-Thiocyano-anisole, m.p. 35°, gives 2-nitro-4-thiocyano-anisole, m.p. 106°, with nitric acid. 4-Thiocyano-phenetole, m.p. 48°. **Thiocyano-cresols**: 5-thiocyano-*o*-cresol, m.p. 71°, 5-thiocyano-*m*-cresol, m.p. 76°, 5-thiocyano-*p*-cresol, m.p. 105°. The last-named compound rearranges during

formation to a cyclic compound, CH<sub>3</sub>[4]C<sub>6</sub>H<sub>3</sub> $\begin{matrix} [1] \\ [2] \end{matrix} \begin{matrix} \diagup \text{O} \diagdown \\ \diagdown \text{S} \diagup \end{matrix} \text{C:NH}$ . 6-Thiocyano-thymol, m.p. 105° (*Kaufmann*, Ber. 59, 187; Ar. Pharm. 267, 192). **Thiocyano-pyrocatechol**, see p. 222.

### Trihydric Phenols

All three isomeric trihydroxy-benzenes are known. They are pyrogallol, phloroglucinol, and hydroxy-hydroquinone. A special

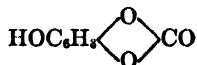
method of formation of the polyhydroxy-benzenes consists of the hydrolysis of polyamino-benzenes. This is particularly suitable for the preparation of phloroglucinols or *sym*-trihydroxybenzenes.

**Pyrogallol**,  $C_6H_3(1,2,3)(OH)_3$ , m.p.  $132^\circ$ , is formed when gallic acid (pyrogallol carboxylic acid),  $COOH[1]C_6H_2[3,4,5](OH)_3$ , is heated by itself. It loses carbon dioxide. This was first observed by *Scheele* in 1786. A better method is to heat gallic acid with water to  $210^\circ$ . Pyrogallol is also obtained from haematoxylin, and from the two *p*-chlorophenol disulphonic acids, by fusion with caustic potash. It forms lustrous white leaflets or needles, readily soluble in water, but less in alcohol and ether. The alkaline solution very readily absorbs oxygen. The first product of this reaction, especially if the alkali used is barium hydroxide, is *hexahydroxy-diphenyl*,  $(HO)_3C_6H_2.C_6H_2(OH)_3$  (*Harries*, Ber. 35, 2954). Subsequently it breaks down to carbon dioxide, acetic acid, and some brown-coloured products. It is used in gas analysis for the determination of oxygen, and in photography as a developer. Pyrogallol rapidly reduces salts of mercury, silver, and gold, with precipitation of the metals, while it itself is oxidised to acetic and oxalic acids.

Pyrogallol gives a blue colour with a solution containing ferrous and ferric ions. The colour turns brown on standing. An excess of ferric salt oxidises it to purpuro-gallin, a dye, which can also be obtained by electrolytic oxidation of pyrogallol (*Perkin*, Proc. 19, 58; 20, 18; J. 85, 243). The course of this reaction has not yet been fully elucidated. Lead acetate gives a white precipitate of  $C_6H_3(OH)_3OPbOOH$ , with pyrogallol. Antimony is completely precipitated from solution as pyrogallate. With iodine solution, pyrogallol gives a purple-red colour in either aqueous or alcoholic solution. Gallic and tannic acids give a similar coloration.

*Ethers*.—1-Methyl ether, m.p.  $41^\circ$ , b.p.  $147^\circ$  (16 mm.); 2-methyl ether, m.p.  $87^\circ$ , b.p.  $155^\circ$  (24 mm.). The 1,3-dimethyl ether, m.p.  $26^\circ$ , b.p.  $251^\circ$ , occurs in beech-wood tar, and can be obtained by the partial hydrolysis of the trimethyl ether. It is interesting to note that in the latter reaction the central methoxyl group is hydrolysed first, even with sodium ethoxide (*Thoms*, Ber. 44, 2135). Oxidising agents convert the dimethyl ether into *coerulignon* (p. 503), a diphenyl derivative. For the reaction of this ether with benzoyl chloride, see *Mauthner*, J. pr. 133, 126. 1,2-Dimethyl ether, b.p.  $235^\circ$  (*Herzig*, Mo. 25, 501, 808). Trimethyl ether, m.p.  $47^\circ$ , b.p.  $236^\circ$  (*Will*, Ber. 21, 607, 2020). The ethyl, diethyl, and triethyl ethers melt at  $95^\circ$ ,  $79^\circ$ , and  $39^\circ$ , respectively. For unsaturated ethers and their Claisen rearrangements, see *Hurd*, Am. 57, 1731.

The syrupy *dimethyl acetate* gives a quinone,  $C_6H_2(OMe)_2O_2$ , with chromic acid. The crystalline triacetate melts at  $164^\circ$  (*Vosswinkel*, Ber. 45, 1246). It loses an acetyl group when heated with  $ZnCl_2$  to  $145^\circ$ , and is converted into gallo-acetophenone (p. 352) (*Heller*, Ber. 45, 2389). **Pyrogallol carbonate**,



m.p.  $133^\circ$ , is obtained by the action of carbonyl chloride in pyridine on pyrogallol, and can be reconverted into pyrogallol by the action of hot water (*Einhorn*, Ber. 37, 106).

**Trichloro-pyrogallol**,  $C_6Cl_3(OH)_3$ , m.p.  $177^\circ$  (decomp.) (*Hantzsch*, Ber. 20, 2035). **4-Bromo-pyrogallol**,  $Br[4]C_6H_2[1,2,3](OH)_3$ , m.p.  $140^\circ$  (decomp.); **4,6-dibromo-pyrogallol**,  $Br_2[4,6]C_6H[1,2,3](OH)_3$ , m.p.  $158^\circ$  (decomp.), are obtained by brominating pyrogallol carbonate. **Tribromo-pyrogallol**,  $C_6Br_3(OH)_3$ , m.p.  $168$ – $170^\circ$ , obtained by the action of bromine on pyrogallol, gives xanthogallol (Vol. II, p. 59) when heated with bromine (*Théuer*, Ann. 245, 335).

4-Nitro- and 4,6-dinitro-pyrogallol, m.p. 162° and 208°, respectively, have been obtained by nitrating pyrogallol carbonate. They can be reduced to the corresponding amino-compounds, which are substances which can be readily oxidised, and which, on boiling with water or dilute acids, give 1,2,3,4-tetrahydroxy- and pentahydroxy-benzene, respectively (*Einhorn*, Ber. 37, 114).

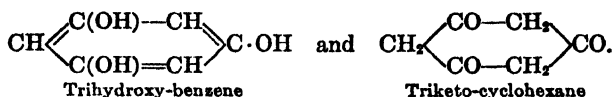
**Methyl-pyrogallol-dimethyl ether**,  $\text{MeC}_6\text{H}_2(\text{OH})(\text{OMe})_2$ , m.p. 36°, b.p. 265°, occurs in beech-wood tar. 1-Methyl-3,4,5-pyrogallol-4,5-dimethyl ether, *iridol*, m.p. 57°, b.p. 249°, is obtained by distillation of iridic acid,  $\text{COOH} \cdot \text{CH}_2\text{C}_6\text{H}_2(\text{OH})(\text{OMe})_2$  (Ber. 26, 2018). The 3,5-dimethyl ether is an oil; its acetate, m.p. 70°, is found in wood-tar (*Schulles*, Ber. 69, 1870). 1-Ethyl-3,4,5-pyrogallol, m.p. 86–87°, is prepared by reducing 3,4,5-trimethyl-gallo-acetophenone by Clemmensen's method, and removing the methyl groups with HI (*Mauthner*, J. pr. 129, 281). 1-Propyl-3,4,5-pyrogallol, *hydroxydivarin*, m.p. 78°, occurs in the Chinese drug, *Ramalina divaricata*, and has been synthesised from 3,4,5-trimethoxybenzoyl-acetic ester by methylation, ketonic decomposition, reduction by Clemmensen's method, and removal of methyl groups by HI (J. pr. 112, 218). **Propyl-pyrogallol dimethyl ether**, *picamar*,  $\text{C}_3\text{H}_7 \cdot \text{C}_6\text{H}_2(\text{OH})(\text{OMe})_2$ , m.p. 285°, was detected in beech-wood tar by *Reichenbach* (Ann. 8, 224; *Hoffmann*, Ber. 11, 329). 5-Amino-pyrogallol-trimethyl ether,  $(\text{MeO})_3\text{C}_6\text{H}_2\text{NH}_2$ , m.p. 114°, is obtained from trimethyl-gallamide (*Graebe*, Ann. 340, 224; cf. Vol. II, p. 362). 4-*n*-Alkyl-pyrogallol ethers (from  $\text{C}_2\text{H}_5$  to  $\text{C}_7\text{H}_{15}$ ) have been prepared from the corresponding ketones by Clemmensen's method (*Hart*, Am. 58, 1957).

**Phloroglucinol**,  $\text{C}_6\text{H}_3[1,3,5](\text{OH})_3$ , m.p. 218° when rapidly heated. This compound was first obtained by *Hlasiwetz* by the hydrolysis of phloretin (1855). It is also obtained from *quercetin*, *hesperidin*, and other glucosides (Vol. II, p. 361). It is the parent substance of the active principles of the *filix* group (*Akamatsu*, Acta Kyoto, 1922). Many resins, e.g., catechu, kino, gamboge, dragon's blood, etc., give it when fused with potash. Phloroglucinol is formed when resorcinol, orcinol, and benzene trisulphonic acid are fused with caustic soda (*Tiemann*, Will, Ber. 14, 954; Will, 18, 1323). It is also formed by the action of acetone on malonyl chloride, when HCl is eliminated. The reaction is violent (*Komminos*, Bull. 23, 449). When synthetic phloroglucinol-dicarboxylic ester (*q.v.*) is hydrolysed, it loses carbon dioxide and phloroglucinol is formed (*Baeyer*, Ber. 18, 3454). The best method of preparation is from *sym*-triamino-benzene (p. 109), which is not itself isolated, but the solution of its double salt with stannous chloride, obtained by reducing trinitrobenzene, is directly hydrolysed by boiling with hydrochloric acid.

Homologous phloroglucinols have been made by similar methods (*Weidel*, Mo. 19, 223; 21, 13). Mono-, di-, and trimethyl-phloroglucinols,  $\text{C}_6\text{H}_2(\text{Me})(\text{OH})_3$ ,  $\text{C}_6\text{H}(\text{Me})_2(\text{OH})_2$ ,  $\text{C}_6\text{Me}_3(\text{OH})$ , m.p. 215°, 163°, and 184°, respectively.

Phloroglucinol crystallises in large prisms with  $2\text{H}_2\text{O}$ , and effloresces in air. It loses all its water of crystallisation at 100°, and melts and sublimes at 218°. It has a sweetish taste. It dissolves readily in water, alcohol, and ether. Its aqueous solution gives a violet colour with ferric chloride, and a precipitate with lead acetate. When chlorine is passed through its aqueous solution, it decomposes into dichloroacetic acid and tetrachloro-acetone (p. 32), hexachloro-cyclohexane being an intermediate product. Homologous phloroglucinols react similarly. (*Schneider*, Mo. 20, 401). For the action of bromine see *Zincke*, Ber. 23, 1707. On reduction, phloroglucite, or *sym*-trihydroxy-cyclohexane is produced (*Wislicenus*, Ber. 27, 357).

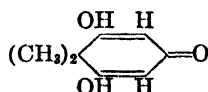
Phloroglucinol behaves like a trihydric phenol,  $\text{C}_6\text{H}_3(\text{OH})_3$ , in most of its reactions, e.g., in reacting with phenyl isocyanate (cf. *Dieckmann*, Ber. 37, 4637, but cf. *Michael*, Ber. 38, 48), and in acylation. On the other hand, it forms a trioxime with hydroxylamine (see below), so that it may also be considered as a triketone, 1,3,5-triketo-cyclohexane (*Baeyer*, Ber. 19, 159).



In order to explain the formation of the trioxime, it might be assumed that the 1,3,5-trihydroxy-benzene formula represents an unstable *pseudo*-form of phloroglucinol. With sodium bisulphite, phloroglucinol forms a compound containing one molecule of each component. See *Fuchs*, Ber. 54, 245, for the behavior of this substance towards acids and alkalis.

When phloroglucinol is methylated by means of methyl iodide and alkali, it is the keto-form which reacts. The final product is **hexamethyl-phloroglucinol**, or **hexamethyl-triketto-cyclohexane**,  $\text{C}_6(\text{Me})_6\text{O}_3$ , m.p.  $80^\circ$ , b.p.  $248^\circ$  (*Herzig*, Mo. 32, 491). This compound is also obtained by methylation of the homologous methyl-phloroglucinols, and decomposes when acted upon by concentrated hydrochloric acid into diisopropyl-ketone and isobutyric acid. When phloroglucinol is acetylated, a triacetate is formed, which gives triacetyl-triketto-cyclohexane, m.p.  $156^\circ$ , when heated with zinc chloride to  $130^\circ$ , or by the action of aluminium chloride at ordinary temperatures (*Heller*, Ber. 42, 2736; 45, 318; *Mauthner*, J. pr. 139, 293). The condensation of phloroglucinol and its homologues with salicylaldehyde is peculiar, part of the molecule reacting in the keto- and part in the hydroxy-form. The products are *fluorones* (Vol. IV) (*Weidel*, Mo. 21, 62).

Phloroglucinol combines readily with formaldehyde to form *methylene-bis-phloroglucinol*,  $\text{CH}_2[\text{C}_6\text{H}_2(\text{OH})_3]_2$ , a derivative of diphenyl-methane, which when reduced with zinc dust and sodium hydroxide decomposes into phloroglucinol, methyl-phloroglucinol, and a little dimethyl- and trimethyl-phloroglucinol. It is closely related to filixic acid, obtained from *Aspidium filix mas*, which on reduction with the above reagents gives phloroglucinol, methyl-, dimethyl-, and trimethyl-phloroglucinols, and *butyryl-filixic acid*. The last, on prolonged reduction with the above reagents, decomposes into *n*-butyric acid and filixinic acid, which is presumably *gem*-dimethyl-dihydroxy-keto-dihydrobenzene (Vol. II, p. 118):



(*Boehm*, Ann. 307, 249; 318, 230; 329, 269).

**Phloroglucinol trioxime**,  $\text{C}_6\text{H}_6(\text{NOH})_3$ , is a crystalline powder, which explodes on heating to  $155^\circ$ . Phloroglucinol adds on to phenylhydrazine in the same way as oxalacetic and diketosuccinic esters do (p. 151).

**Trinitroso-phloroglucinol**,  $\text{C}_6(\text{NO})_3(\text{OH})_3$  (Ber. 11, 1375), and **trinitro-phloroglucinol**,  $\text{C}_6(\text{NO}_2)_3(\text{OH})_3$ , give on reduction, **triamino-phloroglucinol**,  $\text{C}_6(\text{NH}_2)_3(\text{OH})_3$ , and this gives *croconic acid* (p. 241) when boiled with manganese dioxide and sodium carbonate.

**PHLOROGLUCINOL ETHERS.** These are obtained from the phloroglucinols on treatment with alcohols and HCl, or by methylation with diazomethane or dimethyl sulphate in ether. The **methyl ether**, m.p.  $75-78^\circ$ , b.p.  $213^\circ$  (16 mm.), gives a mononitroso-derivative which can be converted into hydroxy-methoxy-*p*-quinone, and should be regarded as a monoxime of the latter, and a dinitroso-derivative which gives diamino-dihydroxy-anisole on reduction. The **dimethyl ether**, m.p.  $37^\circ$ , b.p.  $172-175^\circ$  (17 mm.), reacts with  $\text{N}_2\text{O}_3$  giving simultaneously an *o*- and a *p*-nitroso-derivative, which can be distinguished as 3,5-dimethoxy-*o*-quinone-oxime, red leaflets, m.p.  $175^\circ$ , and 3,5-dimethoxy-*p*-quinone-oxime, yellow needles, m.p.  $222^\circ$ . The **trimethyl ether**, m.p.  $52^\circ$ , b.p.  $255^\circ$ , can be obtained by decomposing *methyl-dihydrocotoin* with potash. The **triphenyl ether**,  $\text{C}_6\text{H}_5(\text{OPh})_3$ , m.p.  $112^\circ$ , is obtained by heating *sym*-tribromobenzene with potassium phenate in the presence of copper bronze (*Ullmann*, Ann. 350, 102). **Phloroglucinol triacetate**, m.p.  $105^\circ$ ; see above. **Trithio-phloroglucinol**,  $\text{C}_6\text{H}_3(\text{SH})_3$ , m.p.  $58^\circ$ , is obtained by reducing *sym*-benzene-trisulphonic chloride with tin and hydrochloric acid. Triacetate, m.p.  $74^\circ$ ; trimethyl ether, m.p.  $68^\circ$  (*Weidel*, Mo. 21, 15; *Herzig*, Mo. 23, 573 [chlorinated ethers]; 27, 781; *Pollack*, Mo. 23, 947; Ber. 42, 3262).



**HYDROXY-HYDROQUINONES** are obtained by the reduction of hydroxy-quinones. **Hydroxy-hydroquinone**,  $C_6H_2[1,2,4](OH)_3$ , m.p.  $140^\circ$ , is formed, together with tetra- and hexahydroxy-diphenyl, when hydroquinone is fused with potash. The best method of preparing it is to obtain the triacetate, which is readily prepared by heating benzoquinone with acetic anhydride and conc. sulphuric acid (*Thiele*, Ann. 311, 341; Ger. Pat. 101,607).



Sodium amalgam reduces hydroxy-hydroquinone to dihydro-resorcinol (Vol. II, p. 111). Hydroxy-hydroquinone gives a greenish-brown colour with ferric chloride. Its triethyl ether,  $C_6H_2(OEt)_3$ , m.p.  $33^\circ$ , is obtained from triethoxybenzoic acid (from aesculetin), or by the ethylation of hydroxy-hydroquinone, and its trimethyl ether, b.p.  $247^\circ$ , is prepared from methoxyquinone (p. 239), or by the action of dimethyl sulphate on the triacetate (*Bargellini*, Gazz. 40, II, 342). See *Thiele*, Ber. 34, 2837, for nitro-, and halogeno-hydroxy-hydroquinones (*Barth*, Mo. 5, 589; *Will*, Ber. 20, 1133; *Brezina*, Mo. 22, 590).

**Hydroquinone monomercaptan**,  $C_6H_2(OH)_2SH$ , m.p.  $120^\circ$ , is obtained in the decomposition of *hydroquinone-thiosulphuric acid*,  $C_6H_2(OH)_2S \cdot SO_2H$ , and other sulphur derivatives of hydroquinone, themselves obtained by the action of sodium thiosulphate and other thio-acids on benzoquinone. It is oxidised by iodine to **hydroquinone disulphide**,  $C_6H_2(OH)_2S_2$ , m.p.  $183^\circ$  (Ger. Pat. 170,070). **3,4-Dimethoxy-phenoxy-acetic acid**, *decarboxy-risic acid*,  $(MeO)_2[3,4]C_6H_2OCH_2COOH$  (p. 371), m.p.  $116-117^\circ$  is a degradation product of *rotenone*, obtained from *Derris elliptica* (*La Forge*, Am. 53, 3896).

### Tetrahydric Phenols

All three isomeric tetrahydroxybenzenes are known.

(1) *v*-**Tetrahydroxybenzene**, *apionol*,  $C_6H_2[1,2,3,4](OH)_4$ , needles, m.p.  $161^\circ$ , is obtained by boiling amino-pyrogallol hydrochloride with water (p. 230). Its alkaline solution does not absorb oxygen (*Einhorn*, Ber. 37, 119). **Tetramethyl ether**, m.p.  $87.5^\circ$ ; **tetra-acetate**, m.p.  $142^\circ$  (*Wessely*, Mo. 60, 161). **1,4-Dimethoxy-2,3-dihydroxybenzene**, *dimethyl-apionol*, is obtained by the action of potash on parsley apiolic acid (p. 455), m.p.  $106^\circ$ , b.p.  $298^\circ$ ; **1,2-dimethoxy-3,4-dihydroxybenzene**, obtained from dill apiolic acid, is a liquid. **Tetramethyl-apionol**,  $C_6H_2(OMe)_4$ , m.p.  $88.5^\circ$  (*Baker*, J. 1931, 2542). **2,3-Methylene-1,4-dimethyl-apionol**, *apione*,  $C_6H_2(O_2:CH_2)(OMe)_2$ , m.p.  $69^\circ$ , is prepared by heating parsley apiolic acid, or apione carboxylic acid with dilute sulphuric acid (*Ciamician*, Ber. 24, 2608; 29, 1806). Dill apiol gives an analogous compound, **1,2-methylene-dihydroxy-3,4-dimethoxybenzene**, a liquid. For its synthesis, see *Baker*, loc. cit. **Dihydro-apiol**, m.p.  $25^\circ$ , b.p.  $292^\circ$ , the methylene-dimethyl ether of 1-n-propyl-2,3,4,5-tetrahydroxybenzene, is obtained by reducing *iso-apiol* (p. 455). (2) *as*-**Tetrahydroxybenzene**,  $C_6H_2[1,2,3,5](OH)_4$ , has not yet been obtained pure in any quantity (cf. *de Laire*, Ber. 26, 2029; *Kohner*, Mo. 20, 927). Its monomethyl ether,  $(MeO)[1]C_6H_2[2,3,5](OH)_3$ , *iretol*, m.p.  $186^\circ$ , is formed in the decomposition of *irigenin* with potash, and has been synthesised by reducing methyl picate (p. 201), and replacing the amino-groups by hydroxyl groups. Its **1,3-dimethyl ether**, m.p.  $158^\circ$ , is obtained from **1,3-dimethoxy-2,5-quinone** (p. 239). **1,2,3-Trimethyl ether**, *antiarol*, m.p.  $146^\circ$ , is obtained from 5-amino-pyrogallol-trimethyl ether (p. 230) by the action of dilute sulphuric acid (*Graebe*, Ann. 340, 225), or better, by the partial methylation of the **1,3-dimethyl ether** (*Chapman*, J. 1927, 3015). **Tetramethyl ether**, m.p.  $47^\circ$ , b.p.  $271^\circ$  (*Ciamician*, Ber. 23, 2291; *Bargellini*, Gazz. 45, I, 85). **Tetrahydroxy-m-xylene**,  $C_6[1,3]Me_2(OH)_4$ , m.p.  $189^\circ$ , is produced by the reduction of dihydroxy-m-xyloquinone (p. 240) (*Brunnmayr*, Mo. 21, 1). (3) *sym*-**Tetrahydroxybenzene**,  $C_6H_2[1,2,4,5](OH)_4$ , m.p.  $215-220^\circ$ , is obtained by reducing **1,4-dihydroxy-2,5-quinone** (p. 239) with  $SnCl_2$ ; **1,4-dimethyl ether**, m.p.  $170^\circ$ ; **tetramethyl ether**, m.p.  $102^\circ$  (*Schueler*, Ar. Pharm. 245, 262; *Erdman*, Proc. Roy. Soc. 143, 177). **Tetra-acetyl ester**, m.p.  $217^\circ$  (*Nietzki*, Ber. 21, 2374). For the triacetate of the mono-methyl ether see *Erdman*, loc. cit.

**Dichloro-tetrahydroxybenzene**, *hydro-chloranilic acid*,  $C_6Cl_2(OH)_4$ , is obtained

by the reduction of chloranilic acid (p. 239) with warm aqueous sulphurous acid (*Graebe*, *Ann.* 146, 32). Amino-*sym*-tetrahydroxybenzene is obtained by the action of stannous chloride on nitro-dihydroxy-quinone, and nitroamino-*sym*-tetrahydroxybenzene and diamino-*sym*-tetrahydroxybenzene are obtained from nitranilic acid in a similar manner (p. 239) (*Nietzki*, *Ber.* 18, 502). When boiled with caustic potash, the diamino compound gives ammonia and croconic acid (p. 241), and diamino-dihydroxyquinone on oxidation. For hydro-euthiochromates, see euthiochronic acid, p. 240.

### Pentahydric Phenols

*Pentahydroxybenzene*,  $C_6(OH)_5H$ , colourless crystals, is obtained when diamino-pyrogallol is boiled with water (*Einhorn*, *Ber.* 37, 122); penta-acetate, m.p. 165°. Its diethyl ether,  $C_6H[2,4,6](OH)_3[1,3](OEt)_2$ , is produced by boiling triamino-resorcinol-diethyl ether (p. 223) with water (*Wenzel*, *C.* 1903, II, 829).

### Hexahydric Phenols

The remarkable formation of *potassio-hexahydroxybenzene*, or potassio-carbon monoxide, when carbon monoxide is passed over heated potassium, discovered by *Liebig* in 1834 (*Ann.* 11, 182), has already been mentioned on p. 25, where the methods of building up the benzene ring have been considered. The constitution of this compound was elucidated by *Nietzki* and *Benckiser* in 1885. If the fresh reaction product of carbon monoxide and potassium is treated with hydrochloric acid, hexahydroxybenzene,  $C_6(OH)_6$ , is obtained. It may also be prepared by the reduction of triquinoyl (p. 240) with stannous chloride and hydrochloric acid. It separates in slender, light-grey needles, which turn mauve in air. They do not fuse, and are stable up to about 200°. Hexahydroxybenzene is oxidised by concentrated nitric acid to triquinoyl, and when heated with acetic acid and sodium acetate, it is converted into its hexa-acetyl compound,  $C_6(OCOCH_3)_6$ , a crystalline substance melting at 203° (*Nietzki*, *Ber.* 18, 506).

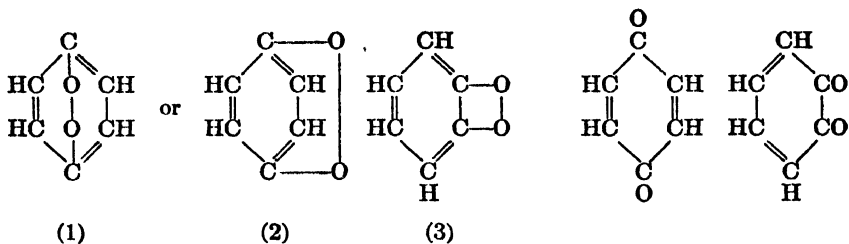
## 8. QUINONES\*

Those compounds in which two nuclear hydrogen atoms are replaced by two oxygen atoms, either in the ortho or para position, are called quinones. *o*- and *p*-Quinones are distinguished, the latter being especially characteristic of the mononuclear aromatic hydrocarbons. *m*-Quinones are not known.

*Constitution*.—The quinones of mononuclear aromatic hydrocarbons may be formulated either as benzene derivatives, assuming the oxygen atoms to be linked to one another, or as derivatives of *o*- or *p*-dihydrobenzene, containing two keto-groups.

If the first constitution is accepted (*Graebe*, 1867, *Z. f. Chem.* 3, 39), the quinones are comparable to peroxides, and they are indeed powerful oxidising agents. On reduction they do not form diglycols of dihydrobenzenes, but give dihydroxybenzenes, true benzene derivatives. The *p*-quinones give hydroquinones, and the *o*-quinones, catechols. By the action of phosphorus pentachloride each oxygen atom is replaced by one chlorine atom. The formation of a monoxime and a di-oxime is put forward as evidence for the keto-formulation (*Fittig*, 1863, *Ann.* 180, 23). In addition, *p*-quinone will add on two or four atoms of bromine (*Nietzki*, *Ber.* 23, 3141). Most chemists regard nitrosophenol as quinone-monoxime (p. 203). The following are the formulae suggested for *o*- and *p*-quinone:

\* *Julius Schmidt*, Chinone und chinoide Verbindungen. Enkesche Sammlung Bd. XI. Stuttgart, 1907.



Peroxide or benzenoid formulae for *o*- and *p*-quinone  
(Graebe)

Diketone or quinoid formulae  
(Fittig)

The first two formulae are no longer regarded as possible. Evidence from X-ray structure indicates that substituents in the benzene nucleus are always situated outside the ring and not inside. In this case, there would hardly be room to accommodate two oxygen atoms within the ring. It is also impossible for the oxygen atoms to be placed on one side of the ring, as *p*-quinone has a zero dipole moment. A peroxidic linkage between the two oxygen atoms, each of which is attached to the benzene ring in its plane and along its axis in the para-position is out of the question, as such a linkage supposes a distance between the oxygen atoms of about one-third the usual value. These arguments, however, do not all apply in the case of *o*-quinone. The peroxide formula (3) which has been assigned to one of the isomeric forms of this substance (see below) appears to be possible. Fittig's formula for *p*-quinone is further supported by the ability of the compound to form addition compounds (Haack, J. pr. 82, 548), shown in the formation of molecular compounds, and in the Diels-Alder reaction, and by its physical properties, especially its parachor (cf. Sugden, Parachor and Valency, London, 1930). At present the diketone formula is generally accepted.

***o*-QUINONES.** The *o*-quinones are much less stable than the para-compounds. It was only in 1904 that Willstätter succeeded in preparing the simplest *o*-quinone, although its chloro- and bromo-derivatives had been prepared earlier (Zincke).

***o*-Benzoquinone**,  $C_6H_4[1,2]O_2$ , is formed by the gentle oxidation of catechol (p. 219) with silver oxide and ether (Willstätter, Ber. 37, 4744). It exists in two forms (Willstätter, Ber. 41, 2580). When freshly prepared it forms colourless prisms, but these soon change to the more stable form, bright red plates, decomposing when heated to 60–70°. Chemically the two forms are identical. The compound is a strong oxidising agent, liberating iodine from acidified potassium iodide. When reduced with sulphur dioxide they give catechol.

Although Willstätter regarded the colourless form as a peroxide, and the red form as a diketone, Kehrman (Ber. 46, 3009) does not regard them as isomerides, but as dimorphous modifications which differ in crystalline form, but not in solution, and are therefore represented by the same formula. Since the two formulae only differ in the arrangement of valencies, with slight differences in the spacing of the atoms, this presents an interesting case on the border line between polymorphism and isomorphism. Unlike *p*-quinone, *o*-quinone is odourless, and not volatile, thus resembling to a greater extent the *o*-quinones of condensed ring systems, such as  $\beta$ -naphthoquinone, and phenanthraquinone.

**1,2-Dimethyl-4,5-benzoquinone**,  $(CH_3)_2[1,2]C_6H_2[4,5]O_2$ , long red needles, is formed by the oxidation of 5-hydroxy-4-amino-1,2-dimethyl-benzene with potassium dichromate and sulphuric acid. **3-Chloro-*o*-quinone**, m.p. about 68° (decomp.) forms prisms, bright yellow or red in colour, according to thickness. It is prepared by the action of lead dioxide on *o*-chloro-catechol in ether-ligroin mixture. **4-Chloro-*o*-quinone**, m.p. 78° (decomp.) is also bright yellow in thin layers and dark red in thick ones. It is obtained by the action of silver oxide and sodium sulphate on *p*-chloro-catechol in ether (Willstätter, Ber. 44, 2182). **Tetrachloro-*o*-quinone**,  $C_6Cl_4[1,2]O_2$ , m.p. 131°, and **tetrabromo-*o*-quinone**,  $C_6Br_4[1,2]O_2$ , m.p. 150°, are obtained by the action of chlorine and bromine, respectively, on catechol dissolved in acetic acid (Zincke, Ber. 20, 1776). **Tetrachloro-benzoquinone** reacts with aniline to give first, **dianilino-dichloro-*o*-quinone**,  $C_6Cl_2(NHPh)_2O_2$ , m.p. 195°, and by further action, **dianilino-monochloroquinone-anil**,  $C_6HCl(NHPh)_2(O):NPh$ , m.p. 180°. The latter seems to

be a derivative of *p*-quinone, since it is reduced by sulphur dioxide to dianilino-*p*-quinone-anil (p. 247). Tetrabromo-*o*-benzoquinone forms similar compounds with aniline. There is a strong tendency for the halogen-*o*-benzoquinones to form addition products with the most diverse compounds. Thus, tetrabromo-*o*-benzoquinone combines with methyl alcohol to form a very stable compound,  $(C_6Br_4O_2)_2MeOH$ , m.p.  $261^\circ$ , which can be acetylated (*Loring Jackson*, Ber. 35, 3851; 36, 454; 38, 4103). When nitric acid acts on tetrachloro- or tetrabromo-*o*-quinone, the ring is broken, and  $\alpha,\alpha$ -dihydroxy- $\beta,\beta$ -dinitro- $\gamma,\gamma,\delta,\delta$ -tetrahalogeno- $\Delta^2$ -*n*-hexene-carboxylic acid is formed (*Zincke*, Ann. 435, 135).

Homologous chloro-*o*-quinones are obtained by the action of chlorine on *o*-diamine hydrochlorides. *o*-Diketo-chlorides are first formed. These can be reduced to chloro-*o*-hydroxybenzenes, and subsequently oxidised to chloro-*o*-quinones (*Zincke*, Ber. 27, 560).

*Dioximes* of *o*-benzoquinone and several of its homologues (p. 241) have been obtained from *o*-dinitroso-benzenes (p. 67) by reduction. *o*-Nitrosophenol (p. 202) should be regarded as a monoxime of *o*-benzoquinone.

***p*-QUINONES.** Quinone, benzoquinone,  $C_6H_4O_2$ , m.p.  $116^\circ$ , was first obtained by *Woskresensky* by oxidation of *quinic acid* (Vol. II, p. 135), a hexahydro-tetrahydroxy-benzoic acid, with manganese dioxide and sulphuric acid. *Woskresensky* called it *quinoyl*, but the accepted name, quinone, was suggested by *Berzelius* (*Jahresb.* 19, 407).

Quinone is obtained when benzene is oxidised, either electrolytically or with silver peroxide (*Kämpf*, Ber. 38, 3964; *J. pr.* 83, 329), or more conveniently, from *p*-dihydroxybenzene, hydroquinone, or its methyl ether, by oxidation with ferric chloride. Many *p*-derivatives of benzene, *e.g.*, *p*-phenylene diamine, sulphanilic acid, *p*-amino-azobenzene, *p*-aminophenol, *p*-phenol sulphonic acid, *p*-diamino-diphenyl or benzidine, give quinone on oxidation. The usual oxidising agent is potassium dichromate and sulphuric acid. It is often prepared by oxidising aniline with sodium dichromate and sulphuric acid (*cf. Nietzki*, Ber. 20, 2283, for practical details), or aniline is treated alternately with manganese dioxide and chromic acid (Ger. Pat. 396,354). A black dye, "aniline black," is an intermediate product in this process (*Willstätter*, Ber. 42, 2147). Quinone is also formed by the oxidation of quinitol (Vol. II, p. 102). It is prepared from hydroquinone in 89% yield by oxidation with sodium chlorate and sulphuric acid in the presence of vanadium pentoxide (*Underwood*, Org. Synth. 16, 73).

Quinone crystallises in golden-yellow prisms. It has a peculiar, penetrating pungent smell. It sublimes readily. Its dipole moment is 0.67 D. It is poisonous and affects the skin (*Furuta*, Bull. Tokyo 4). It is volatile with steam, and is freely soluble in warm water, alcohol, and ether. When exposed to sunlight it undergoes a change, and it will combine in sunlight with acetaldehyde and benzaldehyde to form *dihydroxy-acetophenone* and *dihydroxy-benzophenone*, respectively (*Klinger*, Ber. 31, 1214). Quinone liberates iodine from an acidified solution of potassium iodide, and can be titrated by making use of this reaction (*Valeur*, C.r. 129, 552; *Willstätter*, Ber. 43, 1171). Sulphur dioxide, or zinc and hydrochloric acid, reduce it, giving first an addition product of quinone and hydroquinone (see below) called *quinhydrone*, and this, when reduced with nascent hydrogen, gives hydroquinone. Hydrogen in the presence of finely divided nickel at

180–190°, reduces it to hydroquinone, but at a lower temperature, six more hydrogen atoms are taken up, and 1,4-cyclohexanediol (Vol. II, p. 111) is formed (*Sabatier*, C.r. **146**, 457). It is reduced quantitatively even in the cold by titanous chloride and hydrochloric acid to hydroquinone (*Knecht*, Ber. **43**, 3455). It is detected by means of a solution of ferrous sulphate and ammonium thiocyanate, acidified with sulphuric acid, which gives a red colour with quinone, owing to the oxidation of the ferrous salt to ferric (*Mörner*, Z. physiol. Chem. **78**, 306). For its physical properties, see *Garner*, J. **1927**, 2877 (parachor); *Anderson*, Am. **54**, 3064.

Concentrated nitric acid dissolves quinone in the cold, but at higher temperatures it is oxidised to oxalic and hydrocyanic acids. Silver peroxide breaks it down to maleic acid and carbon dioxide (p. 29; *Kämpf*, Ber. **39**, 3715). Quinone combines with bromine to give *quinone-di-* and *-tetra-bromides*, m.p. 86° and 170–175°. The hydrogen compound corresponding to quinone tetrabromide is *p*-cyclohexane-dione (Vol. II, p. 111); this has been obtained from *succino-succinic ester*. Quinone combines with acetic anhydride, in presence of concentrated sulphuric acid, giving hydroxy-hydroquinone triacetate (p. 232).

Quinone is converted by phosphorus pentachloride into *p*-dichlorobenzene, and hydroxylamine hydrochloride gives *quinone monoxime*, *p*-nitroso-phenol, and *quinone dioxime* (p. 241). Phenylhydrazine reduces it to hydroquinone, and  $\alpha$ -alkyl-phenylhydrazines reduce it in a similar way, being themselves converted into tetrazenes (p. 165), but nitro- and  $\alpha$ -acyl-phenylhydrazines give *quinone monohydrazones* (p. 244). The nuclear hydrogen atoms of quinone are relatively easily replaced, with or without reduction to hydroquinone. With hydrocyanic acid, *dicyano-hydroquinone* is formed,  $C_6H_2[1,4](OH)_2[2,3](CN)_2$ . Quinone combines with benzene sulphinic acids to form *dihydroxy-diphenyl-sulphone*,  $PhSO_2C_6H_2(OH)_2$ . This is a general reaction of quinoid substances (*cf.* p. 180). With neutral sodium sulphite, quinone forms quantitatively hydroquinone-monosulphonate, which is partially hydrolysed and decomposed to hydroquinone and hydroxyquinone (*Pinnow*, J. pr. **89**, 536).

Thio-acids of the general formula  $RSH$ , where  $R$  is an acid radical, such as thiosulphuric, monothio-carboxylic, xanthic, thiocyanic, *etc.*, acids, combine with quinone to give sulphur derivatives of hydroxy-hydroquinone:  $C_6H_2(OH)_2S-SO_2H$ ,  $C_6H_2(OH)_2S-COPh$ ,  $C_6H_2(OH)_2S-CS-OPh$ , *etc.* (Ger. Pat. 175,070). With phenyl carbinols, compounds such as  $C_6H_2O_2(CHPh)_2$  are formed, with elimination of water; these compounds belong to the polynuclear aromatic series. With aniline, quinone gives *anilino-p*-quinone, m.p. 119–120°, but in alcoholic solution, *2,5-dianilino-quinone*, m.p. 345°, is formed. Nitrilines couple in a similar way (*Suida*, Ann. **416**, 113). In carbon disulphide solution, potassium hydrogen sulphide gives with quinone the potassium salt of *benzoquinone-oxonium hydrosulphide*, an oxonium derivative that is formulated  $O: \langle \text{benzene ring} \rangle : O \begin{smallmatrix} H \\ \diagup \\ SK \end{smallmatrix}$ . It

is a greenish-black powder. See *Richter*, Ber. **43**, 3599, for this and other oxonium compounds of *p*-quinone. Quinone forms addition products with pyridine and quinoline salts (*Ortoleva*, Gazz. **33**, I, 164), and with some metallic halides, the products in this case being dark-red in colour (*Meyer*, Ber. **41**, 2568). With hydrogen halides mono- and di-halogeno-hydroquinones are formed (*Posner*, Ann. **336**, 108). When boiled with primary alcohols in the presence of zinc chloride, quinone forms *dialkoxy-quinones* (*Knoevenagel*, Ber. **34**, 3993).

For the condensation of quinones with acetoacetic ester to form coumarone derivatives, see the latter in Vol. IV. For the addition of diazomethane to quinone, see *Pechmann*, Ber. **32**, 2292. For the electrochemical oxidation of quinone to succinic and maleic acids, see *Kämpf*, J. pr. **83**, 329.

**ADDITION PRODUCTS OF PHENOLS AND QUINONES** (*Nietzki*, Ann. **215**, 134). The most important of the addition products of the quinones are those with mono- and di-hydric phenols. In general, quinone combines with two molecules of a monohydric and one of a dihydric phenol, although a number of exceptions are known (*Meyer*, Ber. **42**, 1149; *Siegmund*, J. pr. **92**, 342). These addi-

tion products of quinone with phenol are characterised by their intense colours. In solution they readily dissociate into their components.

**Phenoquinone**,  $C_6H_4O_2 \cdot 2PhOH$ , m.p.  $71^\circ$ , is formed by the combination of phenol with quinone. It volatilises readily, crystallises in red needles, and gives a blue colour with caustic potash, and a green one with barium hydroxide. For addition products with homologues of phenol, see *Biltris*, Belg. 35, 44. When phenols are heated with quinone, with or without the addition of sulphuric acid, no water is lost, and colourless compounds are formed. They differ from the phenoquinones, and appear to be hydroxy-diphenyl ethers, e.g.,  $HOC_6H_4OC_6H_4(OH)_2$ , which is obtained from resorcinol and quinone (*Blumenfeld*, Ber. 30, 2563).

**Thio-phenoquinone**,  $C_6H_4O_2 \cdot 2PhSH$ , is formed in a similar manner to phenoquinone, by the addition of thiophenol to quinone. It forms dark bronze coloured crystals which give a blue colour with sodium hydroxide. On careful oxidation it gives 3,6-dithio-phenyl-quinone,  $(PhS)_2[3,6]C_6H_2[1,4]O_2$ , m.p.  $257^\circ$ , which is readily reduced to 3,6-dithiophenyl-hydroquinone, m.p.  $103^\circ$ . On acetylation, the molecule breaks down and hydroquinone diacetate is formed (*Posner*, Ann. 336, 85). Compounds resembling thio-phenoquinone are obtained from quinone with aliphatic mercaptans.

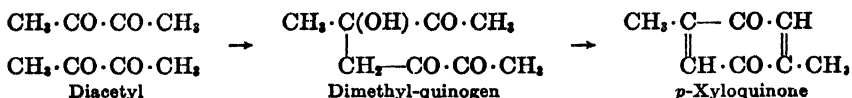
**Quinhydrone**,  $C_6H_4O_2 \cdot C_6H_4(OH)_2$ , m.p.  $171^\circ$  (*Wöhler*, 1844), is formed by the direct union of quinone with hydroquinone. It is an intermediate product in the reduction of quinone and the oxidation of hydroquinone, e.g., with ferric chloride, or by electrolysis (*Liebmann*, Z. Elektrochem. 2, 497). Further oxidation converts it into quinone, and further reduction into hydroquinone. It forms green prisms or leaflets, with a metallic lustre. It has an odour like quinone, melts readily, and dissolves in organic solvents, such as benzene, alcohol, etc., with a yellow colour, dissociating to a large extent into quinone and hydroquinone (*Terrey*, Am. Ch. J. 33, 167). It dissociates completely in boiling water. It is used in the quinhydrone electrode (*Builman*) in the determination of pH values. Formulae have been put forward for this class of compounds by *Loring Jackson*, Ber. 28, 1615, and *Posner*, Ann. 336, 90. They are regarded either as hemiacetal compounds, or as derivatives of dihydroxy-*p*-cyclohexanone. They have been closely studied by *Pfeiffer* (*Organische Molekülverbindungen*, Stuttgart). He found that quinones and related carbonyl compounds, such as maleic and tetrachloro-phthalic anhydrides are capable of forming compounds of this type with phenols and phenol ethers, and even with dimethylaniline, and in some cases with hydrocarbons. The combination of tetrachloroquinone with durene and hexamethyl-benzene are examples. The second component is always a benzene compound, but, contrary to previous opinion, not necessarily one containing either phenolic hydrogen or oxygen, or aromatic hydrogen. The intense colour of these compounds is characteristic, according to *Willstätter*, of the combination of a benzene and a quinoid structure. He calls such systems *merit*- or half-quinoid. This theory has been successfully applied to other coloured compounds such as triphenylmethane and azo-dyes. Wherever a benzoid and a quinoid system combine, an intense colour is likely to appear. These structures resemble those of the free radicals, and have been formulated as such by *Hantzsch*, *Weitz*, and *Michaelis* (Am. 53, 2953). X-ray analysis of quinhydrone indicates that it has the structure

....  ..., the hydrogen atoms being shared by two oxygen atoms (*Foz*, Ann. Espan. 30, 421). Quinhydrone thus appears to be a new type of high polymer.

For quinhydrone from the three trihydroxy-benzenes see *Siegmund*, J. pr. 83, 553.

**HOMOLOGOUS *p*-QUINONES.** These are produced (1) by oxidation of the corresponding *p*-dihydroxy-benzenes (hydroquinones) with ferric chloride, or of the *p*-diamines (*p*-aminophenols), such as amino-thymol, and other para-disubstitution products, with ferric chloride, chromic acid, or manganese dioxide and sulphuric acid. (2) Mono-substituted alkyl-benzenes give *p*-quinones when oxidised with chromic acid. The amino- and hydroxy-alkyl-benzenes (alkyl-phenols) react particularly readily. Thus *o*-toluidine gives toluquinone, and thymol and carvacrol give thymoquinone. In some cases, an alkyl group is replaced by oxygen with the formation of a quinone, e.g., in the oxidation of amino-mesitylene to *m*-xyloquinone (*Noelting*, Ber. 18, 1150), and of pseudo-cumidine to *p*-xyloquinone (p. 340). (3) *p*-Xyloquinone and duroquinone have been synthe-

sised by the action of alcoholic potash on diacetyl and acetyl-propionyl. In this reaction quinogens are first formed, and then *p*-quinones:



*p*-Xyloquinone occurs in beech-wood tar.

**Properties.** The homologues of *p*-benzoquinone are very similar to the parent compound. They are all yellow in colour, and possess an odour similar to that of quinone. They sublime readily, and react chemically like quinone. They form quinhydrones (p. 237), are readily reduced by sulphurous acid to hydroquinones, and combine with hydroxylamine to give nitroso-phenols and quinone-dioximes.

**Toluquinone**,  $\text{CH}_3[\cdot 1]\text{C}_6\text{H}_5[2,5]\text{O}_2$ , m.p. 69° (*Carstanjen*, J. pr. 23, 423)

*o*-Xyloquinone,  $(\text{CH}_3)_2[1,2]\text{C}_6\text{H}_2[3,6]\text{O}_2$ , m.p. 55°

*m*-Xyloquinone,  $(\text{CH}_3)_2[1,3]\text{C}_6\text{H}_2[2,5]\text{O}_2$ , m.p. 72° (*Noelling*, Ber. 18, 1151)

*p*-Xyloquinone, *phlorone*,  $(\text{CH}_3)_2[1,4]\text{C}_6\text{H}_2[2,5]\text{O}_2$ , m.p. 125°

**Ethylbenzoquinone**,  $(\text{C}_2\text{H}_5)[2]\text{C}_6\text{H}_4[1,4]\text{O}_2$ , m.p. 37° (*Clemmensen*, Ber. 47, 56)

**Pseudocumooquinone**,  $(\text{CH}_3)_3[1,2,4]\text{C}_6\text{H}[3,6]\text{O}_2$ , m.p. 32° (*Nietzki*, Ber. 27, 1430)

**Duroquinone**,  $(\text{CH}_3)_4[1,2,4,5]\text{C}_6[3,6]\text{O}_2$ , m.p. 111° (*Willstätter*, Ber. 42, 4161)

**Thymoquinone**,  $(\text{CH}_3)(\text{C}_6\text{H}_7)[1,4]\text{C}_6\text{H}_2[2,5]\text{O}_2$ , m.p. 45°, b.p. 232°

For the electrochemical oxidation of toluquinone, see *Yokoyama*, Bull. Japan, 6, 275. When a solution of thymoquinol in ether is allowed to stand in sunlight for some time, **poly-thymoquinone**, m.p. 200°, separates (*Liebermann*, Ber. 18, 3195). For *diduroquinone* see *Rueggheimer*, Ber. 29, 2176.

**HALOGENO-QUINONES** are obtained from quinones by substitution or by oxidising halogen-hydroquinones.

A mixture of *tri*- and *tetrachloroquinone*, called *chloranil* forms lustrous golden leaflets. It is produced, together with chloropicrin (Vol. I, p. 465) by the action of chlorine, or potassium chlorate and hydrochloric acid (*Brady*, J. 109, 650) or of *aqua regia* (*Kempf*, Ber. 47, 2615) on many benzene derivatives, such as aniline, phenol, and isatin (p. 424). It is most readily obtained from trichloro- or pentachlorophenol by the action of chloro-sulphonic acid, or by the action of fuming sulphuric acid and chlorine (*Schuloff*, Chem.-Ztg. 56, 569). It has been used as an oxidising agent in the manufacture of dyes. *Tri*- and *tetrachloroquinones* are separated from one another by the insolubility of the latter in water. Nitric acid oxidises chlorohydroquinones to chloroquinones (*Graebe*, Ann. 146, 9; *Levy*, Ann. 210, 145; *Kollrepp*, Ann. 234, 14).

**Monochloroquinone**, m.p. 57°

**2,5-Dichloroquinone**, m.p. 161°

**2,6-Dichloroquinone**, m.p. 121°

**Trichloroquinone**, m.p. 169°

**Tetrachloroquinone**, m.p. 290°

(sealed tube)

**Monobromoquinone**, m.p. 55°

**2,5-Dibromoquinone**, m.p. 188°

**2,6-Dibromoquinone**, m.p. 130°

**Tribromoquinone**, m.p. 147°

**Tetrabromoquinone**, m.p. 300°

**Dibromo-diiodoquinone**, m.p. 255°

For 2,3-dihalogeno-quinones, and their conversion into 2,3-dihalogeno-hydroquinones, see *Dimroth*, Ann. 446, 132. For the preparation of tetrachloroquinone free from the trichloro-derivative, see Ger. Pat. 256,034.

Phosphorus pentachloride converts tetrachloroquinone into phosphorus-containing derivatives,  $\text{C}_6\text{Cl}_5\text{OPOCl}_2(?)$ , and finally into hexachlorobenzene (*Zincke*, Ber. 24, 927). It adds on two atoms of chlorine, becoming **hexachloro-*p*-diketo-cyclohexene**, which is broken down by caustic soda into dichloro-maleic acid and trichloroethylene. Potassium hydroxide converts trichloroquinone and tetrachloroquinone into potassium chloranilate (p. 239), and tribromo- and tetrabromoquinone into potassium bromanilate. **3-Chloro-toluquinone**, m.p. 90°, is obtained by introducing the weight of chlorine calculated for the formation of dichloro-cresol into *o*-cresol, and oxidising the product with sodium dichromate and acetic acid (*Kehrmann*, Ber. 48, 2021).

**Amino-quinones.** Amino-quinone is obtained in the form of its acetyl compound,  $C_6H_3O_2(NHCOCH_3)$ , m.p.  $142^\circ$ , by oxidation of 1,3,4-diacetaminophenol. 1,4,5-Diacetaminophenol gives 2,5-diamino-quinone,  $C_6H_3O_2[2,5]-(NH_2)_2$  (Kehrmann, Ber. 30, 2096; 31, 2390).

**Dichloro-diamino-quinone**, *chloranil-amide*,  $C_6Cl_2(NH_2)_2O_2$ , is obtained from chloranilic acid (see below). When aniline acts on a hot alc. solution of quinone, not only is hydroquinone formed, but also dianilino-quinone, *dianilino-quinone-anil* and *-dianil*, and 2,5-dihydroxy-1,4-quinone (see below).

**Quinone monosulphonic acid**,  $C_6H_3O_2(SO_3H)$ , forms yellow prisms, and is obtained by the oxidation of hydroquinone sulphonic acid, and of the two *p*-aminophenol sulphonic acids, with lead dioxide in sulphuric acid solution. The ammonium salt forms golden plates, which decompose at  $190-195^\circ$  (Schultz, J. pr. 69, 334).

### *Hydroxyquinones and Polyquinoyls*

**HYDROXYQUINONES.** **Methoxy-quinone**,  $MeO[2]C_6H_3:O_2$ , m.p.  $143^\circ$ , is produced by oxidising *o*-amino-anisole with chromic acid, or methoxyhydroquinone with lead dioxide (Erdtman, Proc. Roy. Soc. 143, 177). **Chloranilamic acid**, *dichloramino-hydroxy-quinone*,  $C_6Cl_2(NH_2)OHO_2$ , is obtained from chloranil. 2,3-Dimethoxy-quinone, m.p.  $66^\circ$ , is prepared by oxidising 4-aminopyrogallol-dimethyl ether with chromium trioxide,  $CrO_3$  (Baker, J. 1931, 2542), and 2,6-dimethoxy-quinone,  $(MeO)_2[2,6]C_6H_3O_2$ , is prepared by oxidising pyrogallol or phloroglucinol trimethyl ether (Ciamician, Ber. 26, 784; Graebe, Ann. 340, 238). 2,5-Dihydroxy-quinone,  $(HO)_2[2,5]C_6H_3O_2$ , consists of yellow needles, which sublime at  $210-215^\circ$ , with partial decomposition. It is a dihydric acid, and can be obtained from dihydroxy-quinone-carboxylic acid by heating with hydrochloric acid, by oxidation of diamino-resorcinol (Nietzki, Ber. 21, 2374; Boeniger, Ber. 22, 1285), or by the action of dilute sulphuric acid on dianilino-quinone (Kehrmann, Ber. 23, 904; 31, 2042). It is also obtained by hydrolysis of its ethers. 2,5-Dimethoxy-, diethoxy-, and -dipropoxy-quinones, decomposing at  $220^\circ$ , and melting at  $166^\circ$  and  $167^\circ$ , respectively, are formed from quinone by boiling with the corresponding alcohol, hydroquinone being formed at the same time (Knoevenagel, Ber. 34, 3993). 2,5-Dimethoxyquinone is also produced by the action of nitric acid on 1,2,4,5-tetramethoxy-benzene (Baker, J. 1931, 2542). 2,5-Dihydroxy-quinone is converted into *sym*-tetrahydroxy-benzene (p. 232), by stannous chloride, and into dianilino-quinone (see above) by aniline.

*Substitution products of 2,5-dihydroxy-quinone* have been obtained by starting with tetrachloro- and tetrabromo-quinone, two of the halogen atoms in these compounds being very easily replaced.

**Chloranilic acid**,  $C_6Cl_2(OH)_2O_2$ , is obtained in reddish lustrous scales by the action of acids on potassium chloranilate,  $C_6Cl_2(OK)_2O_2 \cdot H_2O$ , which crystallises in dark red needles, and is difficultly soluble in water. Potassium chloranilate is formed by the action of caustic potash on tri- or tetrachloroquinone. By the action of hypochlorous acid or chlorine on chloranilic acid, tri- or tetrachlorotetraketo-cyclohexane is formed. These change quite readily into trichloro-triketo-cyclopentane, with the intermediate formation of unstable hydroxy-acids (Hantzsch, Ber. 25, 827; Landolt, Ber. 25, 842). For halogenated hydroxyquinones see Zincke, Ann. 437, 86.

**Bromanilic acid**,  $C_6Br_2(OH)_2O_2$ , corresponds to chloranilic acid, and gives with bromine products similar to those obtained by the action of chlorine on chloranilic acid.

**Nitranilic acid**,  $C_6(NO_2)_2O_2(OH)_2$ . This substance crystallises in the hydrated form in golden yellow needles. It melts in its own water of crystallisation, becomes anhydrous at  $100^\circ$ , and detonates at  $170^\circ$  without melting. It is obtained by the action of nitrous acid on quinone or hydroquinone. When nitrous fumes are passed into an ether solution of quinone, the solution being kept cool, nitranilic quinone,  $C_6N_2O_3H_2$ ,  $C_6H_4O_2$ , is formed. This resembles a quinhydrone in structure, and is decomposed by dilute caustic potash into quinone and nitranilic acid (Schmidt, Ber. 33, 3246). The latter is also obtained by the action of sodium nitrite on chloranil, or by the action of fuming nitric acid on diacetyl-hydroquinone dissolved in a mixture of acetic anhydride and glacial acetic acid (Nietzki, Ber. 43, 3458), or on dihydroxyquinone and dihydroxyquinone-dicarboxylic acid.



When nitranilic acid is reduced it gives diamino-tetrahydroxybenzene, which makes it possible to pass from chloranil to triquinoyl (see below) and potassium hexahydroxy-benzene.

**Amino-anilic acid, diamino-dihydroxy-quinone**,  $C_6(NH_2)_2(OH)_2O_2$ , is produced when diamino-tetrahydroxy-benzene is oxidised by air or nitrous acid. It forms reddish-blue needles (*Nietzki*, Ber. 21, 1850). **Cyano-anilic acid, 2,5-dicyano-3,6-dihydroxyquinone**,  $C_6(CN)_2(OH)_2O_2 + 2H_2O$ , is obtained by the action of potassium cyanide on chloranil. It chars on heating. Its solutions in a number of solvents show a strong fluorescence (*Richler*, Ber. 44, 3469).

**Potassium euthiochronate**,  $C_6(SO_3K)_2(OH)_2O_2$ , is obtained from dichloro-quinone disulphonic acid (p. 228).

**Nitro-dihydroxyquinone sulphonic acid**,  $C_6NO_2(OH)_2O_2(SO_3H)$ . The tripotassium salt of this acid is produced by the action of potassium nitrite on potassium dichloro-hydroquinone disulphonate (*Nietzki*, Ber. 38, 453).

**Tetrahydroxyquinone**,  $C_6(OH)_4O_2$ , formerly called dihydrocarboxylic acid, is obtained by atmospheric oxidation of an aqueous solution of hexahydroxybenzene (*Nietzki*, Ber. 18, 507, 1837). It can also be obtained from diamino-dihydroxyquinone (see above) by boiling with hydrochloric acid, and by the action of concentrated nitric acid on inositol. It forms black needles, with a green, metallic lustre. It is a strong dibasic acid.

**Tetrathio-ethylquinone**,  $C_6O_2(SC_2H_5)_4$ , forms colourless prisms, m.p.  $59^\circ$ , and is obtained by the action of sodium mercaptan on chloranil (*Sammis*, Am. 27, 1120).

**HOMOLOGOUS HYDROXYQUINONES** are obtained by acting upon the halogenated homologues of quinone with caustic potash, or by heating amino- or anilino-quinones with alcoholic hydrochloric or sulphuric acid. **Dianilino-toluquinone**, m.p.  $232^\circ$ , gives anilino-hydroxy-toluquinone, decomp. at  $250^\circ$ , and dihydroxy-tolu-quinone,  $CH_3 \cdot C_6H(OH)_2O_2$ , m.p.  $177^\circ$  (*Zincke*, Ber. 16, 1559). **Dihydroxy-m-xyloquinone**,  $C_6(CH_3)_2O_2(OH)_2$ , red flakes, m.p.  $167^\circ$ , is obtained from amino-dimethyl-phloroglucinol (*Brunnmayr*, Mo. 21, 1). **Hydroxy-thymoquinone**,  $(C_6H_7)(CH_3)C_6H(OH)_2O_2$ , m.p.  $166^\circ$ , is obtained from bromo- or methyl-amino-thymoquinone. **Dihydroxy-thymoquinone**, m.p.  $213^\circ$  (*Zincke*, Ber. 14, 95).

**p-DIALKYLATED DIHYDROXY-QUINONES**, such as *p,p'*-dimethyl-dihydroxy-benzoquinone,  $C_6(CH_3)_2[3,6](OH)_2[2,5]O_2[1,4]$ , are formed as by-products in the preparation of homologous oxalacetic esters by condensation of ethyl oxalate with fatty acid esters by means of sodium in ether solution. They form red or yellowish-red compounds, which dissolve in alkalis with a violet colour. On reduction they give homologous tetrahydroxy-benzenes. When boiled with excess of caustic soda, they are split up into homologous succinic acids. *p,p'*-Dimethyl-, diethyl-, and diisopropyl-dihydroxy-benzoquinones melt at  $245^\circ$ ,  $218^\circ$ , and  $154^\circ$ , respectively (*Fichter*, Ann. 361, 363).

**POLYQUINOYL COMPOUNDS.** As already mentioned (p. 235), *Woskresensky* originally called quinone *quinoyl*. *Nietzki* and *Benckiser* used this term in a different sense. They used it for the quinone group  $O_2$ , when they discovered dihydroxy-diquinoyl benzene and triquinoyl benzene to be substances containing more than one quinone group. For the sake of simplicity they abbreviated these names to *dihydroxy-diquinoyl* and *triquinoyl*.

**Dihydroxy-diquinoyl**,  $O_2 \cdot C_6(OH)_4 \cdot O_2$ , or *rhodizonic acid*, is obtained by reducing triquinoyl with sulphurous acid. It forms colourless leaflets which are very readily soluble in water. Its aqueous solutions decompose rapidly. The potassium salt may be obtained by treating the acid with potassium carbonate, and also by washing potassium hexahydroxybenzene with alcohol. It forms dark blue needles, which dissolve in water to give a yellow solution (*Nietzki*, Ber. 18, 513, 1838). For the constitution of rhodizonic acid, see *Nietzki*, Ber. 23, 3140.

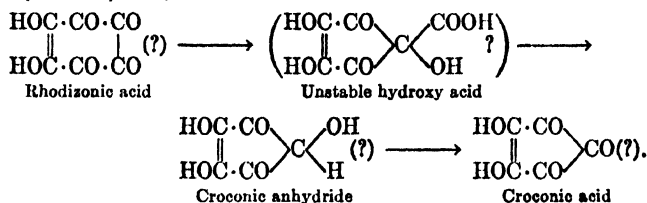
**Triquinoyl**,  $C_6O_6 + 8H_2O$ , is probably *hexaketo-cyclohexane*. It is produced by oxidising dihydroxy-diquinoyl and diamino-tetrahydroxybenzene with nitric acid. It is a white, micro-crystalline powder (*Nietzki*, Ber. 18, 504; 20, 322; *Henle*, Ann. 350, 330). It melts about  $95^\circ$ , losing water and carbon dioxide. It is reduced by stannous chloride to hexahydroxybenzene (p. 233), which is itself oxidised in alkaline solution to tetrahydroxy-quinone,  $C_6(O_2)(OH)_4$  (see above).

Nietzki and Benckiser (1885) discovered the relations between potassium carbon monoxide (potassium hexahydroxy-benzene) and phenol. These are summed up in the following table:

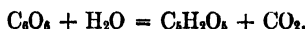
|                              |                           |                         |                           |
|------------------------------|---------------------------|-------------------------|---------------------------|
| Phenol                       | $C_6H_5OH$                | $C_6(OK)_6$             | potassium carbon monoxide |
| Tetrachloroquinone           | $C_6Cl_2Cl_2O_2$          | $C_6(OH)_4(OH)_2(OH)_2$ | hexahydroxy-benzene       |
| Nitrilic acid                | $C_6(NO)_2(OH)_2O_2$      | $C_6(OH)_2(OH)_2O_2$    | tetrahydroxy-quinone      |
| Diamino-tetrahydroxy-benzene | $C_6(NH_2)_4(OH)_2(OH)_2$ | $C_6(OH)_2O_2$          | rhodizonic acid           |
| Diamino-dihydroxy-quinone    | $C_6(NH_2)_2(OH)_2O_2$    | $C_6O_2O_2$             | triquinoyl                |

Pentacarbocyclic compounds are readily formed from triquinoyl and dihydroxy-diquinoyl, and from their parent substances, the hexa-substitution derivatives of benzene, *e.g.*, hexahydroxy-benzene, diamino-tetrahydroxy-benzene, *etc.*

Croconic acid hydride,  $C_6H_4O_4$ , is formed by treating rhodizonic acid with excess of alkali, or croconic acid with hydriodic acid. It is characterised by its barium salt,  $C_6H_2BaO_4 \cdot 2H_2O$ . It is probably formed by the decomposition of an unstable hydroxy-acid, produced by the action of caustic alkali on two of the linked CO groups of rhodizonic acid (*cf.* the benzoic acid rearrangement, p. 556) (Nietzki, Ber. 23, 3136):



Croconic acid,  $C_6O_4(OH)_2 \cdot 3H_2O$ , forms sulphur-yellow leaflets. It loses its water of crystallisation at  $100^\circ$ . It dissolves very readily in water and alcohol. It is obtained by the action of concentrated nitric acid on inositol,  $C_6H_8(OH)_2$  (Vol. II, p. 103), by the action of oxygen at  $80^\circ$  on the sodium salt of tetrahydroxy-quinone, or calcium rhodizonate, carbon dioxide and water being liberated (Gelormini, J. 52, 2483), and by the alkaline oxidation of hexahydroxy-benzene, dihydroxy-diquinoyl, diamino-tetrahydroxy-benzene, *etc.* Croconic hydride, which readily passes into croconic acid, is an intermediate product in these reactions. When triquinoyl is boiled with water, it decomposes into carbon dioxide and croconic acid:



Its potassium salt,  $C_6O_4K_2 \cdot 3H_2O$ , crystallises in orange-yellow needles. Hence the name from saffron (*Gmelin*, 1825).

The so-called *leuconic acid*,  $C_6O_4 \cdot 4H_2O$  (Contardi, Gazz. 51, I, 109), has been shown to be a mixture of croconic acid, rhodizonic acid, tetrahydroquinone, and hexahydroxy-benzene (Gelormini, J. 52, 2483).

### Nitrogen Derivatives of Quinone

The oxygen atoms of quinone can be replaced by  $N(OH)$ ,  $NCl$ ,  $NH$ ,  $NPh$ , and similar groups.

**QUINONE-DIOXIMES.** In connection with the *p*-nitroso-phenols, and in the explanation of Fittig's diketone formula for quinone (p. 202), it was stated that many chemists regard the *p*-nitroso-phenols, produced by the action of hydroxylamine hydrochloride on the *p*-quinones, as quinone monoximes. It is true that the *p*-nitroso-phenols are converted into *p*-quinone dioximes by the action of hydroxylamine hydrochloride. These two classes of compounds can be regarded as constituted according to the peroxide formula for the *p*-quinones (p. 234). *o*-Quinone dioximes are formed by the reduction of *o*-dinitroso-benzenes; they readily eliminate water, passing into anhydrides, the so-called *furazane* derivatives (Zincke, Ann. 307, 28).

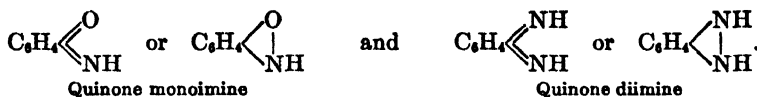
The dioximes combine with acetic anhydride giving diacetyl compounds. *p*-Dinitroso-benzenes (p. 67) are formed by atmospheric oxidation of alkaline solutions of the dioximes. They are oxidised by nitric acid to *p*-dinitrobenzenes (Nietzki, Ber. 20, 978).

***o*-Quinone dioxime**,  $C_6H_4[1,2](NOH)_2$ , small yellow needles, dissolves in alkalis giving a blood-red solution, and is converted into its colourless anhydride,  $C_6H_4-N_2O$ , m.p.  $55^\circ$ , merely on standing, or on warming in alkaline solution (*Hantzsch*, Ber. 40, 4344).

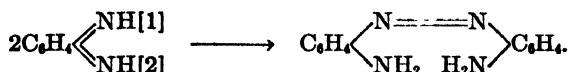
***p*-Quinone dioxime**,  $C_6H_4[1,4](NOH)_2$ , forms colourless, or yellow needles, which decompose at  $240^\circ$ . Toluquinone-dioxime, deflagrates at  $220^\circ$  (*Fischer*, Ber. 21, 679). ***p*-Xyloquinone-dioxime**, melts at about  $272^\circ$  (*Sutkowski*, Ber. 20, 978). **Mono- and di-benzoyl-quinone-dioxime**, see *Tollorici*, Gazz. 33, I, 237.

Dinitro-resorcinol and hydroxylamine give **diquinoyl trioxime**,  $C_6H_2O(NO_2)(NOH)_3$ , and **diquinoyl tetroxime**,  $C_6H_2(NO_2)(NOH)_4$ . When the latter is oxidised with sodium hypochlorite, it gives tetranitroso-benzene (*Nietzki*, Ber. 30, 181; 32, 505).

**QUINONE-IMINES** are to be regarded as diketones, or as peroxides (p. 234), in which the oxygen is replaced by the imino-group ( $:NH$ ), or the alkyl-imino-group ( $:NR$ ), corresponding to the formulae:



They are formed from *p*-aminophenol, or *p*-phenylene diamine by gentle oxidation with silver oxide or lead dioxide in ether solution. The monoamines are bright yellow, and the diamines are colourless, and very unstable. They form coloured picrates (*Kehrmann*, Ber. 56, 2398). They are strong oxidising agents, smell like quinones, and are volatile. When warmed with mineral acids they decompose into ammonia and quinone. When reduced with stannous chloride and hydrochloric acid, or by sulphurous acid, they are reconverted into the original substances, *p*-aminophenol and *p*-phenylene diamine. Owing to the ease of decomposition of the *o*-quinones, the isolation of the *o*-quinone imines, which are probably more unstable, has not yet been carried out. The *o*-quinone-diimine, probably first formed by the oxidation of *o*-phenylene diamine, polymerises at once to *o*-azo-aniline (p. 142) (*Willstätter*, Ber. 38, 2348):

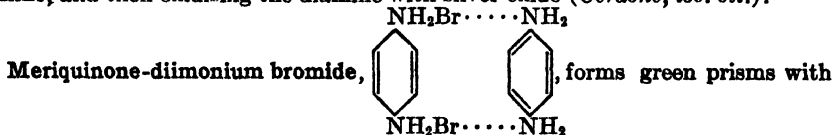


**Quinone-monoimine**,  $O[1]C_6H_4[4]NH$ , forms bright yellow prisms, which quickly turn black in solution when exposed to the light, and decompose in a short time when dry (*Willstätter*, Ber. 37, 4607; *Kehrmann*, Ber. 56, 2398).

**Quinone-monomethyl-imine**,  $O[1]C_6H_4[4]NCH_3$ , is formed by oxidation of *p*-methyl-aminophenol,  $OHC_6H_4NHCH_3$ , with silver oxide, or lead dioxide. It is even more unstable than the unmethylated imine, and deflagrates spontaneously (*Willstätter*, Ber. 38, 2251).

**Quinone-diimine**,  $NH[1]C_6H_4[4]NH$ , m.p. about  $124^\circ$ , is formed by reduction of *p*-quinone-dichlorimine with hydrochloric acid in ether solution. It forms colourless, monoclinic prisms, which quickly turn brown in air (*Kehrmann*, Ber. 56, 2402). It combines with sodium bisulphite to form a mixture of *p*-amino-phenol sulphonic acid, and *p*-phenylene diamine sulphonic acid.

**Toluquinone-monimines**,  $O[1]C_6H_3[2](CH_3)[4]NH$  and  $O[1]C_6H_3[3](CH_3)[4]NH$ , are obtained by oxidising *p*-amino-*o*-cresol and *p*-amino-*m*-cresol, respectively, with silver oxide (*Cordone*, Helv. 7, 956, 964). **Thymoquinone-monoimine**,  $O[4]C_6H_2[1]NH[2]Me[5]C_6H_7$ , m.p.  $74^\circ$  (decomp.) is prepared similarly from *p*-amino-thymol (*Kehrmann*, Ber. 56, 2400). **Thymoquinone-diimine**,  $NH[4]-C_6H_3[1]NH[2]Me[5]C_6H_7$ , is obtained from nitroso-thymol by first making it into a diamine by means of hydroxylamine hydrochloride, reducing this to a diamine, and then oxidising the diamine with silver oxide (*Cordone*, loc. cit.).



a coppery lustre. Its nitrate, which occurs as brass coloured crystals, has been

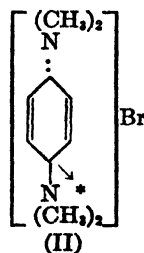
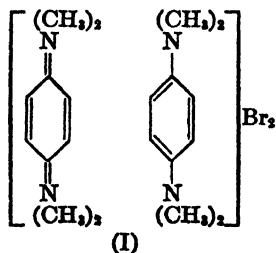
prepared by Piccard (Ann. 381, 351) by treating *p*-phenylene diamine dissolved in glacial acetic acid with bromine and nitric acid or nitrous fumes.

**Quinone-monomethyl-diimine**,  $\text{NH}[1]\text{C}_6\text{H}_4[4]\text{NCH}_3$ , m.p. 64–67°, and **quinone-dimethyl-diimine**,  $\text{CH}_3\text{N}[1]\text{C}_6\text{H}_4[4]\text{NCH}_3$ , m.p. 93°, are obtained, like the simple quinone diimines, by the oxidation of monomethyl- or *sym*-dimethyl-*p*-phenylene diamine. They form almost colourless crystals, but in solution the substances have a pale yellow colour. They are as unstable as quinone-diimine itself (Willstätter, Ber. 38, 2249; 40, 2672). **Quinone-imide ammonium compounds**,  $\text{NH}:\text{C}_6\text{H}_4:\text{NR}'\text{R}''\text{R}'''$ , are obtained by adding alkyl iodides to *p*-acetyl-amino-dialkyl-anilines, and hydrolysing the ammonium salts of the formula  $\text{NH}_2\text{C}_6\text{H}_4\text{N}(\text{R}'\text{R}''\text{R}''')\text{I}$ , produced (Meldola, J. 107, 610).

**as-Quinone dimethyl-diimonium nitrate**,  $\text{NH}:[1]\text{C}_6\text{H}_4[4]:\text{N}(\text{CH}_3)_2\text{NO}_3\cdot\text{HNO}_3$ , is obtained as very unstable light-yellow prisms, by the oxidation of *as*-dimethyl-*p*-phenylene diamine with nitrous fumes. It decomposes rapidly and explodes on heating. It combines with one molecule of its hydro-compound, *as*-dimethyl-*p*-phenylene diamine to form a compound  $[\text{NO}_2\text{NH}_2:\text{C}_6\text{H}_4:\text{N}(\text{CH}_3)_2\text{NO}_3 + \text{NH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]$ , of which the structure resembles that of quinhydrone. It forms green crystals, which dissolve in water with a magenta colour. These interesting compounds are called Wurster's dyes, after their discoverer, and are obtained by the partial oxidation of salts of *as*-dimethyl-*p*-phenylene diamine (Wurster, Ber. 12, 1803, 2071). The corresponding hydrobromide, *meri*-dimethylquinone-diimonium bromide, Wurster's red (Piccard, Ann. 381, 351), m.p. 147° (decomp.), is formed by the action of one atom of bromine on a solution of *as*-dimethyl-*p*-phenylene diamine in glacial acetic acid. It forms green crystals, which give a deep red solution. The latter is bleached by reducing agents with the formation of phenylene diamine. Oxidising agents also bleach the solution, forming the entirely quinoid compound (Willstätter, Ber. 41, 1458).

Analogous blue compounds are obtained by starting with tetramethyl-*p*-phenylene diamine. Unstable oxidation products coloured intense green or blue have also been obtained from *p*-phenylene diamine and dibromo-*p*-phenylene diamine (Wurster, Ber. 12, 1807; Pringsheim, Ber. 38, 3354; Willstätter, Ber. 41, 1458, 1473; Jackson, Am. Ch. J. 31, 209).

These Wurster's dyes are of considerable interest in connection with the relation between colour and chemical constitution. The oxidation level of these salts is intermediate between that of diaminobenzene and quinone-diimine. They can be formulated as binuclear quinhydrone structures, comprising one benzenoid, and one quinoid ring, as shown by formula (I), where Wurster's blue is taken as an example. The oxidation level of the quinoid system exceeds that of the benzenoid system by two equivalents, i.e., the former contains two electrons less than the latter. A second method of formulating the combined system as a single ring, containing one electron less than a benzene system, is shown in (II). The arrow indicates a free valency, i.e., one unpaired electron. (II) represents a free radical, and it might be objected that Wurster's dyes do not behave like free radicals. However, this may be due to the fact that the radicals in this case are ions. The recent work of Michaelis (Am. 53, 2953) seems to indicate that they are mononuclear, and provides strong evidence in favour of formula (II). The problem may be put briefly as follows: is a meriquinoid structure necessarily a combination of a benzenoid and a quinoid ring, or can it exist as a mononuclear system of intermediate level of oxidation?



\* Free valency or unpaired electron.

**Amino-quinone-imine**,  $\text{NH}_2[2]\text{C}_6\text{H}_3[1]\text{O}[4]\text{NH}$ , and its homologues are formed by the oxidation of 2,4-diamino-phenols with ferric chloride. The dichromate forms greenish-black, lustrous grains which dissolve in water giving a red solution (*Kehrmann*, Ber. 39, 3437). **Diamino-quinone-imine**,  $(\text{NH}_2)_2\text{C}_6\text{H}_2(\text{O})(\text{NH})$  (?), is obtained from triamino-phenol (*Hepp*, Ann. 215, 351).

**QUINONE-CHLORIMINES**. These are produced from *p*-amino-phenols and *p*-phenylene diamines by oxidation with an aqueous solution of bleaching powder. Reduction converts them back to *p*-amino-phenols or *p*-phenylene diamines. The monochloroimines give the indophenol dyestuffs with phenols and tertiary anilines (p. 245). They combine with one molecule of hydroquinone to give dark-green compounds of quinhydrone nature (*Knorr*, Ber. 43, 798). **Quinone-monochloroimine**,  $\text{O}[1]\text{C}_6\text{H}_4[4]\text{NCl}$ , m.p.  $85^\circ$ , is also formed in the oxidation of aniline with hypochlorous acid (*Bamberger*, Ann. 311, 78). It exists as golden-yellow crystals, which volatilise readily with steam, and smell like quinone. It is readily soluble in water, alcohol, and ether, and when boiled with water it decomposes into ammonium chloride and quinone (*Schmitt*, J. pr. 23, 435). **Quinone-dichloroimine**,  $\text{C}_6\text{H}_4[1,4](\text{N}_2\text{Cl}_2)$ , crystallises in needles, which deflagrate at  $124^\circ$  (*Krause*, Ber. 12, 47). **Trichloro-quinone-chlorimine**, m.p.  $118^\circ$  (*Schmitt*, J. pr. 24, 429). **Bromo-quinone-chlorimine**, m.p.  $60^\circ$  (decomp.) (*Raiford*, Am. 46, 417). **Dibromo-quinone-chlorimine**, m.p.  $80^\circ$  (*Möhlau*, Ber. 16, 2845).

**QUINONE-PHENYLHYDRAZONES**. Phenylhydrazine and alkylated phenylhydrazines are oxidised by quinone, but *o*-nitro- and *o,p*-dinitro-phenylhydrazine give condensation products, which may be regarded as *p*-hydroxy-azo-compounds, as they are identical with the products obtained by coupling diazotised *o*-nitro- or *o,p*-dinitraniline with phenol (*Borsche*, Ann. 357, 171). True quinone phenylhydrazones are formed, on the other hand, with  $\alpha$ -acetyl- and -benzoyl-phenylhydrazine. **Quinone acetyl- and -benzoyl-phenylhydrazones**,  $\text{O}:\text{C}_6\text{H}_4:\text{N}:\text{NR}$  ( $\text{C}_6\text{H}_5$ ,  $\text{R} = \text{COCH}_3$  or  $\text{COC}_6\text{H}_5$ ), melt at  $118^\circ$  and  $171^\circ$ , respectively. They very readily pass into the acylated *p*-hydroxy-azo-compounds,  $\text{ROC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_5$  (*Willstätter*, Ber. 40, 1432). This reaction is of special importance in connection with the determination of the constitution of hydroxy-azo-compounds (p. 210). *o*-Quinone-benzoyl-phenylhydrazone (?) gives *o*-hydroxy-azobenzene on hydrolysis (*McPherson*, Am. 31, 281).

**QUINONE-OXIME HYDRAZONES** are formed by the action of benzoylhydrazine and benzoyl-phenylhydrazine on nitrosophenols (p. 202). **Quinone-oxime benzoyl-hydrazone**,  $(\text{HON}):\text{C}_6\text{H}_4:\text{NNH}:\text{COC}_6\text{H}_5$ , melts at  $210^\circ$  (decomp.). **Quinone-oxime benzoyl-phenylhydrazone**,  $(\text{HON}):\text{C}_6\text{H}_4:\text{NN}(\text{CO}:\text{C}_6\text{H}_5)_2$ , m.p.  $177^\circ$ , gives *p*-nitro-azobenzene when boiled with nitric acid (*Borsche*, Ann. 343, 176). *o*-Quinone phenylhydrazone,  $\text{C}_6\text{H}_5\text{NH}\cdot\text{N}\cdot$



(p. 210), was formerly thought to be a hydroxy-azo-compound,  $\text{PhN}:\text{N}[1]-\text{C}_6\text{H}_4[2]\text{OH}$  (*Burawoy*, Ann. 509, 60; 521, 298).

**QUINONE-SEMICARBAZONES AND AMINO-GUANIDONES**. The quinones react more readily with semicarbazide and with amino-guanidine than with phenylhydrazine. **Quinone-mono- and -bi-semicarbazone**,  $\text{C}_6\text{H}_4\text{O}(\text{NNHCO}:\text{NH}_2)$  and  $\text{C}_6\text{H}_4(\text{NNHCONH}_2)_2$ , m.p.  $171^\circ$  and  $243^\circ$ , respectively, are obtained from quinone and semicarbazide hydrochloride. **Quinone-mono- and -bis-amino-guanidone**,  $\text{C}_6\text{H}_4\text{O}[\text{NNHC}(\text{NH})\text{NH}_2]$ , and  $\text{C}_6\text{H}_4[\text{NNHC}(\text{NH})\text{NH}_2]_2$ , are obtained by the action of amino-guanidine nitrate on quinone in the presence of nitric acid (*Thiele*, Ann. 302, 311). The quinone-mono-semicarbazone and -mono-amino-guanidone are probably hydroxy-azo compounds (*Borsche*, Ann. 334, 1666).

**QUINONE-AZINES**. *p*-Quinone-azine,  $\text{O}[4]\text{C}_6\text{H}_3[1]\text{N}\cdot\text{N}[1]\text{C}_6\text{H}_4[4]\text{O}$ , deflagrates at  $158^\circ$ . It is formed by oxidation of *p*-azo-phenol (p. 210) with silver oxide and lead dioxide in ether solution. It is obtained in the form of dark orange prisms, or dark yellow rhombohedral flakes. It is stable in air, and is odourless, and non-volatile. When reduced with sulphurous acid or phenylhydrazine it is converted into *p*-azo-phenol, but stannous chloride and hydrochloric acid reduce it to *p*-amido-phenol. It combines with one molecule of *p*-azo-phenol, forming a compound resembling quinhydrone, which crystallises in blue-black needles, m.p.

182°. The same compound is obtained by direct oxidation of *p*-azo-phenol. *o*- and *m*-Azo-phenols do not yield quinone-azines (*Willstätter*, Ber. 39, 3482).

**QUINONE-DIAZIDES.** It has already been pointed out in connection with the diazo-salts of the *o*- and *p*-aminophenols that the corresponding diazo-hydroxides readily pass into yellow anhydrides related to the quinones, probably to be regarded as *o*- and *p*-quinone-diazides,  $\text{N}_2\text{C}_6\text{H}_4\text{:O}$  (p. 208). Similar behaviour is shown by the diazonium salts of *p*-amino-diphenylamine,  $\text{NH}_2\text{C}_6\text{H}_4\text{-NHC}_6\text{H}_5$ , which, on treatment with ammonia, form *p*-quinone-diazide-anil,  $\text{N}_2\text{C}_6\text{H}_4\text{:NC}_6\text{H}_5$  (*Hantzsch*, Ber. 35, 888).

**Quinone-phenyl-monoimine**, *quinone mono-anil*,  $\text{C}_6\text{H}_4(\text{ONPh})$ , m.p. 97°, forms fiery red crystals. It is formed by oxidation of *p*-hydroxy-diphenylamine in benzene solution with mercuric oxide, and when reduced it reverts to this compound (*Bandrowski*, Mo. 9, 157).

**INDOPHENOLS AND INDOANILINES.** These compounds are obtained from quinone-mono-anil or quinone-phenyl-imine by replacing the *p*-hydrogen atom of the anil group by an OH or  $\text{NH}_2$  group. They are dyes. Like many members of this class, they are decolourised on reduction, the resulting compounds being called leuco-compounds. These are *p*-di-substituted diphenylamines (for nomenclature, see *Möhlau*, Ann. 289, 90).

**INDOPHENOLS** are formed (1) by condensing phenols, or phenol ethers, in which the *p*-position is free, with *p*-nitroso-phenol or quinone chlorimine, using 70% sulphuric acid or concentrated hydrochloric acid as condensing agents. They may also be obtained by the action of nitric acid, or sodium nitrite and perchloric acid, on phenol ethers (*Kehrmann*, Ber. 54, 2427, 2435). (2) By oxidising a mixture of a *p*-aminophenol and a phenol. They dissolve in alcohol giving red or brown solutions, and resemble the phenols in character. Their alkali-metal and ammonium salts give blue aqueous solutions. They are decomposed by dilute acids giving quinones and *p*-aminophenols. These products can enter into secondary reactions and form hydroquinones and dihydroxy-anilido-quinones (*Heller*, Ann. 418, 259).

**Quinone-phenolimine**, *indophenol*,  $\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_4\text{OH})$ , m.p. 160°, forms brown

leaflets with a metallic lustre, and is readily soluble in alcohol giving a red solution. The sodium salt is blue, and is obtained by oxidising a mixture of phenol and *p*-aminophenol in alkaline solution with sodium hypochlorite at  $-10^\circ$ . The free quinone-phenolimine can then be liberated by the addition of acetic acid. It is also obtained by the action of hot caustic soda on phenol blue (p. 246) (*Möhlau*, Ber. 18, 2916). The chief product of its decomposition is hydroquinone (*Heller*, Ann. 392, 16), and it gives colourless *p*-dihydroxy-diphenylamine (p. 207) on reduction. It can be re-formed from the latter by oxidation with mercuric oxide (*Schneider*, Ber. 32, 689).

**Dibromo-quinone-phenolimine**,  $\text{C}_6\text{H}_2\text{Br}_2\text{N}(\text{C}_6\text{H}_4\text{OH})$ , obtained from dibromo-

quinone-chlorimine, is more stable than quinone-phenolimine. Free dibromo-quinone-phenolimine crystallises in dark red prisms, having a metallic lustre. It dissolves in alcohol and ether with a magenta colour. It is decomposed by concentrated mineral acids into dibromo-aminophenol, and quinone. **Indophenol-**

**N-oxide**,  $\text{C}_6\text{H}_4\text{N}(\text{O})\text{C}_6\text{H}_4\text{OH}$ , is produced as reddish-brown lancets by the

action of a mixture of nitric and sulphuric acid in acetic acid on phenol. It dissolves in mineral acids with a reddish-violet colouration. It chars without a well-defined melting point. Its benzoate, orange to brown leaflets, melts at  $174.3^\circ$  (*Meyer*, Ber. 54, 337).

The **INDOANILINES** are produced (1) by condensation of *p*-nitrosophenol or quinone-chlorimine with dimethylaniline; (2) by the action of nitroso- and nitro-dimethylaniline on phenol in alkaline solution, especially in the presence of reducing agents (*Witt*, 1879); (3) by the oxidation in alkaline solution (with sodium hypochlorite) of a mixture of a *p*-phenylene diamine (or its derivative) with a phenol, or a *p*-aminophenol with a primary mono-amine, or by means of lead dioxide or manganese dioxide in the presence of disodium hydrogen phosphate

(Nietzki, 1877) (*Bayrac*, Bull. [3], 11, 1131; Ger. Pats. 171,028 and 179,294/5).

Indoanilines are weak bases. They are fairly stable towards alkalis, and form colourless salts with acids. On prolonged action of acids, they are readily decomposed into quinones and *p*-phenylene diamines. On reduction, they add on two atoms of hydrogen, forming leuco-compounds (amino-hydroxy-diphenylamines, p. 207), from which the indoanilines are easily reformed by oxidation in alkaline solution, mere exposure to the air being sufficient. The free indoanilines are deep-blue, and can be used as dyes. For this purpose, they are converted into their leuco-compounds, which are soluble in alkalis, and the fabric is impregnated or printed with this solution. Oxidation, by exposure to air, or with potassium bichromate, develops the colour on the fabric.

Quinone-aniline-imine,  $C_6H_4 \begin{smallmatrix} \diagup N \cdot C_6H_5NH_2 \\ \diagdown O \end{smallmatrix}$ , is a violet dye formed in the oxidation of *p*-phenylene diamine and phenol.

Quinone-dimethylaniline-imine, *phenol blue*,  $C_6H_4 \begin{smallmatrix} \diagup N \cdot C_6H_4N(CH_3)_2 \\ \diagdown O \end{smallmatrix}$ , m.p.

167°, obtained from *as*-dimethyl-*p*-phenylene diamine and phenol, is greenish blue in colour, and dissolves in acids giving a blue solution. When boiled with caustic soda it loses dimethylamine and is converted into quinone-phenolimine. It is decomposed by sulphuric acid into quinone and dimethyl-*p*-phenylene diamine. This is a general reaction, and has been used in some cases for the preparation of quinones (*Bayrac*, Bull. [3], 11, 1129; *Möhlau*, Ann. 289, 90).

**QUINONE-PHENYL-DIIMINES.** Quinone-monophenyl-diimine, *quinone-imide-anil*,  $C_6H_4N:C_6H_4:NH$ , forms light yellow prisms, m.p. 89°, and is obtained by oxidation of *p*-amino-diphenylamine (p. 107), with silver oxide or lead dioxide in ether solution. It is also formed, together with quinone-mono-anil, by gentle oxidation of aniline in an aqueous alkaline solution. Water decomposes it, even in the cold, into ammonia and quinone-mono-anil, and when heated with dilute sulphuric acid, it is converted into quinone. In the presence of mineral acids it readily dimerises to form the green dye, *Willstätter's emeraldin*. This is also formed when *p*-amino-diphenylamine is oxidised in acid solution with ferric chloride or hydrogen peroxide, and also by reduction of nitrobenzene in a hydrofluosilicic acid solution, the substance first formed being *p*-amino-diphenylamine. The free base obtained from emeraldin, the so-called *azurin*, m.p. 165°, forms deep blue prisms, and probably has the constitution  $C_6H_5NH \cdot C_6H_4NH \cdot C_6H_4N:C_6H_4:NH$ . When oxidised by lead dioxide in benzene solution, both *azurin* and emeraldin, which are semi-quinoid in structure, pass into the doubly-quinoid *red imine*,  $C_6H_4N:C_6H_4N:C_6H_4N:C_6H_4:NH$ . Like quinone-monophenyl-di-imine, this compound polymerises, under suitable conditions, to a black dye called *aniline black* (*Willstätter*, Ber. 40, 2655; 42, 4123).

**Aniline black\*** is one of the oldest known organic dyestuffs, and is remarkable for its permanence. It is formed by oxidation of aniline salts (p. 76), or *p*-phenylene diamine salts (p. 107), with potassium dichromate and sulphuric acid, ammonium persulphate, or potassium chlorate, in the presence of oxygen carriers, such as copper sulphate, potassium ferrocyanide, ammonium vanadate, etc., or of organic carriers, such as the azo- or nitroso-derivatives of organic bases, or azo-, azoxy-, and hydrazo-benzene, etc.

In cotton dyeing, aniline black is produced on the fabric, by printing the fabric with a mixture of an aniline salt, and one of the above oxidising agents, and then developing the dye by steaming at a low temperature.

Aniline black is related to the red oxidation product of *Willstätter's emeraldin*, the connection being similar to that between emeraldin and quinone monophenyl-diimine. It cannot be regarded as a single compound. It consists of a mixture of triple- and quadruple-quinoid compounds, the amount of each varying with the extent of oxidation, as the compounds are produced in stages by the oxidation of the aniline or *p*-phenylene diamine. According to *A. G. Green*, the stages in the oxidation are as follows (J. 97, 2388):

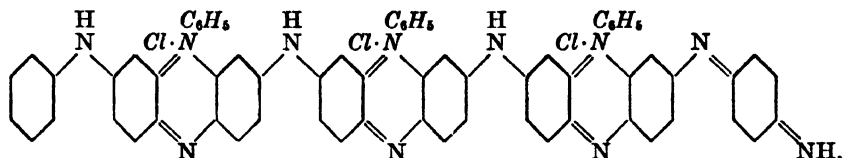
\* *E. Noetling and A. Lehne*, Anilinschwarz und seine Anwendung in Färberei und Zeugdruck. 3rd ed., Springer, Berlin, 1908.

- I.  $C_6H_5NHC_6H_4NHC_6H_4NHC_6H_4NHC_6H_4NHC_6H_4NHCH_2N:C_6H_4:NH$   
 Proto-emeraldin  
 $(C_6H_5NHC_6H_4NHC_6H_4NHC_6H_4NHC_6H_4NHC_6H_4NHC_6H_4NHCH_2N:C_6H_4:NH)$   
 Leuco-proto-emeraldin
- II.  $C_6H_5NHC_6H_4NHC_6H_4NHC_6H_4NHC_6H_4N:C_6H_4:NC_6H_4N:C_6H_4:NH$   
 Green's emeraldin
- III.  $C_6H_5NHC_6H_4NHC_6H_4N:C_6H_4:NC_6H_4N:C_6H_4:NC_6H_4N:C_6H_4:NH$   
 Nigraniline
- IV.  $C_6H_5N:C_6H_4:NC_6H_4N:C_6H_4:NC_6H_4N:C_6H_4:NC_6H_4N:C_6H_4:NH$   
 Pernigraniline

The number of quinoid groups in the oxidation products of aniline can be determined by the phenylhydrazine method of *Willstätter* and *Cramer* (Ber. 43, 2976; cf. *Green*, Ber. 44, 2570), the volume of nitrogen evolved being measured.

When heated with dilute sulphuric acid, one-eighth of the total nitrogen of aniline black is split off as ammonia, the imino-group being replaced by oxygen. This is accompanied by an increase in the depth of the colour. These oxygen-containing substances are contained in aniline black in proportions varying with the method of preparation. Powerful oxidising agents, such as chromic acid, or lead dioxide and sulphuric acid, convert aniline black almost entirely into quinone (*Willstätter*, Ber. 42, 2147, 4118).

When a mixture of nigraniline and pernigraniline is subjected to further oxidation in the presence of aniline, three more molecules of aniline attach themselves to the molecule, and true aniline black is formed (*Green*, Ber. 46, 3769). This substance has a phenyl-azonium structure, represented by the following graphic formula, in which the three molecules of aniline attached at the final stage are indicated in italics:



**Quinone-diphenyl-diimine**, *diphenyl-p-azo-phenylene*, *quinone-dianil*,  $C_{16}H_{12}N_2$  ( $NC_6H_5$ )<sub>2</sub>, m.p. 176–180°, is obtained by the oxidation of diphenylamine (p. 84), and diphenyl-*p*-phenylene diamine. When reduced, quinone dianil gives diphenyl-*p*-phenylene diamine, to which it is related in the same way as quinone is to hydroquinone.

Two phenyl-amino groups may be introduced into the benzene residue of quinone-anil and quinone-dianil with the same ease as into quinone itself, which as mentioned above, gives dianilino-quinone and hydroquinone when its alcoholic solution is boiled with aniline. If acetic acid is present, **dianilino-quinone-anil**,  $(C_6H_5NH)_2C_6H_2(O)(NC_6H_5)$ , m.p. 202°, is formed as brownish-red needles. The same compound is formed when quinone-mono-anil is heated with aniline, but is accompanied by *p*-hydroxy-diphenylamine. It is also produced by oxidising aniline with hydrogen peroxide in a feebly acid solution.

**Dianilino-quinone-dianil**, *azophenine*,  $(C_6H_5NH)_2C_6H_2(NC_6H_5)_2$ , m.p. 241°, forms garnet-red flakes. It is produced (1) by heating quinone-dianil with aniline; (2) by melting quinone with aniline and aniline hydrochloride; (3) by the action of aniline on amino-azobenzene, *p*-nitrosophenol, or *p*-nitroso-diphenylamine. When heated it is converted into *fluorindine* (Vol. IV). The quinone-dianils are important intermediates in the manufacture of induline dyes (*Zincke*, Ber. 18, 787; *Fischer*, Ber. 20, 2480; 21, 683; 23, 2791; 25, 2731; *Brandrowski*, Mo. 9, 414; *Hewitt*, Ber. 31, 1789).

**INDAMINES.** The indamines are derived from quinone-phenyl-diimines in the same way as indoanilines are from quinone-monoanils. They are closely related to *p*-diamino-diphenylamine, which is the leuco-derivative of the simplest indamine, being obtained from it by reduction.

Indamines are formed: (1) by the action of nitroso-dimethyl-aniline on anilines or *m*-diamines (*Witt*, Ber. 12, 933); (2) by oxidising a mixture of *p*-phenylene



diamine and an aniline in neutral solution, and in the cold (*Nietzki*, Ber. 28, 2974); (3) by oxidising a mixture of *m*-phenylene diamine and *p*-aminophenol hydrochloride in dilute alkaline solution (*Ullmann*, Ber. 45, 3437). They are weak bases, forming blue- or green-coloured salts with acids, but with an excess of acid they are readily decomposed into quinone and the diamine. On account of their instability they have no practical use, but are important as intermediate products in the manufacture of thionine and safranin dyes, into which they can be readily converted. For the connection between the indophenols, indanilines, and indamines to the dyes of the oxazine, thiazine, and diazine series, such as resorufin, methylene blue, the indulines and safranines, see Vol. IV.

The simplest indamine is **phenylene blue**,  $C_6H_4 \begin{smallmatrix} \nwarrow N(C_6H_4NH_2) \\ \nearrow NH \end{smallmatrix}$ , which is obtained by the oxidation of *p*-phenylene diamine with aniline. Its salts are greenish-blue in colour. It gives diamino-diphenylamine on reduction. Its tetramethyl hydrochloride is

**Dimethyl-phenylene green**, *Bindschedler's green*,  $N \begin{smallmatrix} \nwarrow C_6H_4N(CH_3)_2 \\ \nearrow C_6H_4=N(CH_3)_2Cl \end{smallmatrix}$ ,

obtained by the oxidation of dimethyl-*p*-phenylene diamine with dimethylaniline. Its salts give a green aqueous solution. On reduction it gives tetramethyl-diamino-diphenylamine, and when digested with dilute acids it is converted into quinone and dimethylaniline (*Bindschedler*, Ber. 16, 865; *Nietzki*, Ber. 17, 223). On standing with caustic soda, dimethylamine splits off, and phenol blue is produced, and by the loss of more dimethylamine, quinone-phenol-imine (p. 245) is formed (*Möhlau*, Ber. 18, 2915). Phenol blue is also obtained by oxidising tetramethyl-diamino-diphenylamine with potassium ferricyanide in alkaline solution (*Wieland*, Ber. 48, 1078).

**Toluylene blue**,  $C_{15}H_{11}N_4Cl = N \begin{smallmatrix} \nwarrow [1]C_6H_2[3]CH_3[4,6](NH_2)_2 \\ \nearrow [1]C_6H_4[4]=N(CH_3)_2Cl \end{smallmatrix}$ , is produced from

ordinary toluylene diamine (p. 107) by oxidising a mixture of it with dimethyl-*p*-phenylene diamine, or by the action of nitroso-dimethylaniline hydrochloride. Its salts with one equivalent of acid are of a beautiful blue colour, and are decolourised by excess of mineral acid with formation of the diacid salts. It is converted into the azine dye, toluylene red, on boiling with water.

The connection between the indamines and indoanilines and indophenol is shown by the fact that it is possible to convert the simplest indamine into quinone-aniline-imine, and the latter into quinone-phenol-imine (*Möhlau*, Ber. 16, 2843; 18, 2915).

A large number of representatives of the indophenols, indoanilines, and indamines containing the naphthalene residue are known. A few of them, such as *naphthol blue* or "indophenol," are used industrially (*Möhlau*, Ber. 18, 2916).

For quinoid sulphur compounds, see *Zincke*, Ber. 40, 3039; 41, 902.

## 9. THE PHENYL PARAFFIN ALCOHOLS AND THEIR OXIDATION PRODUCTS

In the preceding sections those classes of derivatives of mono-nuclear aromatic hydrocarbons which are formed by the replacement of hydrogen atoms in benzene itself, or of the benzene residue of alkyl-benzenes, by atoms of other elements or groups of atoms, have been described. The classes dealt with were: *halogen* substitution products (p. 49); *nitrogen* derivatives of benzene hydrocarbons (p. 56); *aromatic phosphorus*, *arsenic*, *antimony*, *bismuth*, *boron*, and *silicon* compounds (p. 166); the *phenyl metal* compounds (p. 170); the *sulphonic acids*, and their related compounds (p. 173); the *phenols* (p. 183), and the *quinones* (p. 233).

The classes of substances to be dealt with in the succeeding sections

are those obtained by the replacement of hydrogen atoms of the alkyl groups in alkyl benzenes. As in the case of the aliphatic series, the oxygen derivatives will be regarded as the principal or fundamental compounds. With each group of oxygen compounds are described their derivatives in which all or some of the carbon valencies linked to oxygen in the fundamental compounds are linked to halogen, sulphur, or nitrogen. As in the case of the aliphatic series, we shall deal first with those compounds in which one carbon atom of the side-chain is linked to oxygen, *viz.*:

(1a) *The monohydric phenyl-paraffin alcohols, and their oxidation products—aldehydes, ketones, and carboxylic acids.* As would be expected, these compounds are very similar, as regards the reactions of their functional groups, to the monohydric aliphatic alcohols, and their oxidation products. They are therefore regarded as phenyl substitution products of aliphatic compounds, and are named accordingly.

Each of the alkyl-benzene derivatives constitutes a parent substance from which numerous compounds are derived in the same manner as substituted products from benzene itself. In general, the derivatives of phenyl-aliphatic compounds which are substituted in the ring, will be dealt with after the corresponding principal compounds, as far as they deserve mention. The hydroxyl derivatives of monohydric aromatic alcohols, however, which contain one or more hydroxyl groups attached to the ring, and their oxidation products, which possess both phenolic and alcoholic properties, will be dealt with as a separate group.

(1b) *Monohydric hydroxyphenyl paraffin alcohols and their oxidation products.* Then follow:

(2) *Polyhydric phenyl paraffin alcohols, in which only one hydroxyl group is linked to each side-chain, and their oxidation products; and finally*

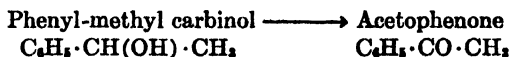
(3) *Polyhydric phenyl paraffin alcohols, in which more than one hydroxyl group is attached to a side-chain, and their oxidation products.*

In subsequent sections the mononuclear benzene derivatives with unsaturated side-chains are dealt with.

## (1a) MONOHYDRIC PHENYL PARAFFIN ALCOHOLS AND THEIR OXIDATION PRODUCTS

### 1. The Monohydric Phenyl Paraffin Alcohols

The *true alcohols* of the benzene class are produced by the introduction of one hydroxyl group into the alkyl residue of an alkyl-benzene. There are *primary*, *secondary*, and *tertiary* alcohols. On oxidation, primary alcohols yield *aldehydes* and *carboxylic acids*, and secondary alcohols, *ketones*.



*Formation.*—Benzyl alcohol and its homologues resemble ethyl alcohol by their similar methods of formation: (1) They are formed when benzyl halides, such as

benzyl chloride, are hydrolysed. The hydrolysis can be effected by water alone (*Niederist*, Ann. 196, 353), by a mixture of water and lead oxide (*Lauth*, Ann. 143, 81), or by aqueous potassium carbonate. The chlorides can also be converted into acetates, and the latter can be hydrolysed.

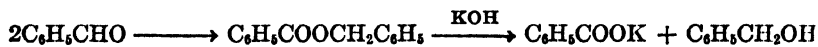
(2) Primary amines (the reduction products of aromatic nitriles), give alcohols when treated with nitrous acid; cumobenzyl alcohol, and hemimellibenzyl alcohol, for example, are prepared in this way.

(3) The alcohols can also be obtained by reduction of the corresponding aldehydes and ketones with nascent hydrogen, preferably in the presence of catalysts (*Skita*, Ber. 48, 1685).

(4a) Ethyl-, isopropyl-, and similar alkyl-benzenes yield secondary and tertiary aromatic alcohols on catalytic oxidation (Ger. Pat. 522,255).

(4b) The magnesium compounds of benzyl halides and their homologues react with oxygen, giving rise to the alcohols; thus *p*-cumyl chloride,  $C_6H_5 \cdot C_6H_4 \cdot CH_2Cl$ , gives  $C_6H_5 \cdot C_6H_4 \cdot CH_2OH$ , *p*-cumyl alcohol (*Bert*, Bull. 37, 1577).

(5) When aromatic aldehydes are treated with alcoholic potash, phenyl-paraffin alcohols and the corresponding carboxylic acids are formed simultaneously. This is known as *Cannizzaro's reaction*. It is rarely observed with paraffin alcohols (*Meyer*, Ber. 14, 2394; *Raikov*, C. 1902, I, 1212). Two molecules of benzaldehyde give one molecule of benzyl alcohol and one of potassium benzoate, benzyl benzoate being probably formed as an intermediate:



(*Titschenko*, J. pr. 86, 322; *Kohn*, Proc. 15, 194).

(6a) By electrolytic reduction of aromatic carboxylic acids or esters, dissolved in alcoholic sulphuric acid. A high cathodic overvoltage is required. When esters are used, the corresponding ethers are formed simultaneously; thus, from methyl benzoate, benzyl alcohol and benzyl-methyl ether,  $C_6H_5CH_2OCH_3$ , are formed, and from phenyl benzoate, benzyl-phenyl ether (*Mettler*, Ber. 38, 1745; 39, 2933; *Kling*, C. 1908, II, 1863; *Fichter*, Helv. 12, 821).

(6b) Alcohols are also obtained by reducing esters of phenyl-fatty acids, other than benzoic and phenyl-glycidic esters, with sodium and ethyl- or amyl alcohol (Ger. Pat. 164,294).

(6c) By reduction of amides of aromatic carboxylic acids whose carboxyl group is linked to the nucleus, with sodium amalgam in acid solution (*Hutchinson*, Ber. 24, 173).

(6d) They are also formed by a process known as "exchange of levels of oxidation," which consists in treating aromatic aldehydes or ketones with a primary aliphatic alcohol, in the presence of a catalyst. The sodium, magnesium, and aluminium compounds of the alcohol in question are usually effective catalysts. A mixture of benzaldehyde, ethyl alcohol, and a metallic ethylate, for example, gives benzyl alcohol and acetaldehyde (*Meerwein*, Ann. 444, 221; *Ponndorf*, Z. angew. 39, 138; Ger. Pats. 384,351 and 432,850).

(7) Aralkylene oxides,  $Ar \cdot C \begin{array}{c} \diagup \diagdown \\ \backslash \diagup \end{array} Alk \cdot CH_2$ , are reduced catalytically to primary alcohols,  $Ar \cdot CHAlk \cdot CH_2OH$  (Br. Pat. 320,424).

(8) Reduction of unsaturated alcohols gives alcohols of this series; thus, cinnamyl alcohol,  $PhCH:CH \cdot CH_2OH$ , is reduced to hydrocinnamyl alcohol,  $PhCH_2 \cdot CH_2 \cdot CH_2OH$ .

(9) Nuclear synthesis is brought about by the action of alkyl-metal compounds on aldehydes, ketones, esters, acid chlorides, and halogen-hydrins: (a) Phenyl magnesium bromide gives phenyl-dimethyl carbinol,  $PhC(OH)(CH_3)_2$ . (b) Aromatic aldehydes, ketones, esters, and chlorides give secondary and tertiary phenyl paraffin alcohols with zinc alkyls, and still better with magnesium alkyl halides (Vol. I, p. 219); aliphatic aldehydes and ketones also give secondary and tertiary phenyl paraffin alcohols with aralkyl-magnesium halides. The tertiary phenyl paraffin alcohols readily lose water and are converted into olefine-benzenes. (c) Phenyl magnesium bromide and ethylene chlorhydrin give phenyl-ethyl alcohol,  $PhC_2H_5OH$  (*Grignard*, Ann. Lyon, 1901; C.r. 132, 1182; Ann. chim. phys. [8], 10, 23). A modification of these syntheses which avoids the use of ether with the Grignard reagent is described by *Schorygin* (Ber. 64,

2584). A synthesis of alcohols from benzene hydrocarbons, ethylene oxide or chlorhydrin, and aluminium chloride, is suggested in Br. Pat. 398,136; Fr. Pat. 716,604.

**Properties.**—The aromatic alcohols are colourless, oily liquids, some possessing a pleasant odour, or crystalline substances. They show the general properties of alcohols, being oxidised to aldehydes, or ketones, forming ethers, esters, *etc.* The lower members occur in some essential oils and balsams, and are of importance in the perfumery industry. The primary alcohols form compounds with anhydrous calcium chloride, which are decomposed by water, and in this way they can be isolated from mixtures. They also combine with phthalic anhydride giving hydrogen phthalates, which dissolve in sodium carbonate solution. The alcohols give high-boiling boric, phosphorous, and arsenious esters (Br. Pat. 252,570). These esters and the hydrogen phthalates can be used in the identification of the alcohols. The crystalline (di-) phenyl-urethanes may also be used for the same purpose.

The alcohols, particularly the tertiary ones, are readily dehydrated with formation of benzene hydrocarbons. Alcohols of the type  $\text{Ar} \cdot (\text{Alk}) \cdot \text{CH} \cdot \text{CH}_2\text{OH}$ , when dehydrated catalytically, undergo partial rearrangement, the alkyl group migrating to the carbinol carbon. Thus, the chief product is  $\text{Ar} \cdot \text{CH} : \text{CH} \cdot \text{Alk}$ , while the normal product,  $\text{Ar} \cdot (\text{Alk})\text{C} : \text{CH}_2$ , is formed in smaller amounts. Alcohols of the type  $\text{Ar} \cdot \text{CH}(\text{OH}) \cdot \text{Alk}$ , contain an asymmetric carbon atom, and can be resolved into optical antipodes by the usual methods. When they are treated with benzene and aluminium chloride the phenyl group replaces the hydroxyl, and benzene hydrocarbons are formed (*Bodforss*, Ber. 51, 192).

**Benzyl alcohol, phenyl carbinol**,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ , solidifying at  $-15.7^\circ$ , b.p.  $206^\circ$ ,  $d_0$  1.062, is isomeric with the cresols (p. 189). It occurs as the benzoic and cinnamic esters in balsams of Peru and Tolu, and in storax (Ann. 169, 289), as the acetate, and sometimes free in some essential oils, *e.g.*, in oil of jasmine flowers (*Hesse*, Ber. 32, 567). It is obtained by methods (1), (2), (3), (5), (6a), (6b), and (6d), given above, from benzaldehyde, benzyl chloride, benzoic acid, and benzamide. It is usually prepared by reactions (1) and (3). It is a colourless liquid, with a faint aromatic odour. It is difficultly soluble in water, but dissolves readily in alcohol and ether. When oxidised it gives benzoic acid and benzaldehyde. When heated with hydrochloric or hydrobromic acid, the hydroxyl group is replaced by the halogen. Benzoic acid and toluene are formed when benzyl alcohol is distilled with concentrated potash.

**History.**—As early as 1832, *Liebig* and *Wöhler* obtained benzyl alcohol in the course of their famous investigation into the benzoyl radical. They obtained it by treating benzaldehyde with alcoholic potash (Ann. 3, 254, 261). *Cannizzaro*, however, was the first to recognise it, when studying this reaction more closely in 1853.

**HOMOLOGOUS PHENYL PARAFFIN ALCOHOLS.** The primary alcohols are usually prepared by methods (1), (2), (3), (4a), (4b), (5), (6a-d), (7), (8), and (9c); hydrocinnamyl alcohol by method (8), secondary alcohols by method (1), or by reducing ketones according to methods (3) and (4a), and secondary and tertiary alcohols by methods (4a) and (9).

Nuclear homologues of benzyl alcohol are given in the table.

| Homologue                                                                                            | M.p.   | B.p. | Reference                         |
|------------------------------------------------------------------------------------------------------|--------|------|-----------------------------------|
| <i>o</i> -Tolylcarbinol,<br>$\text{CH}_3[2]\text{C}_6\text{H}_4[1]\text{CH}_2\text{OH}$              | 35°    | 223° | <i>Mettler</i> , Ber. 39, 2938    |
| <i>m</i> -Tolylcarbinol,<br>$\text{CH}_3[3]\text{C}_6\text{H}_4[1]\text{CH}_2\text{OH}$              | Liquid | 217° | <i>Colson</i> , Bull. 43, 6       |
| <i>p</i> -Tolylcarbinol,<br>$\text{CH}_3[4]\text{C}_6\text{H}_4[1]\text{CH}_2\text{OH}$              | 60°    | 217° | <i>Cannizzaro</i> , Ann. 124, 255 |
| 2,4-Dimethylbenzyl alcohol,<br>$(\text{CH}_3)_2[2,4]\text{C}_6\text{H}_3[1]\text{CH}_2\text{OH}$     | 22°    | 232° | <i>Hinrichsen</i> , Ber. 21, 3085 |
| 3,5-Mesityl alcohol,<br>$(\text{CH}_3)_2[3,5]\text{C}_6\text{H}_3[1]\text{CH}_2\text{OH}$            | Liquid | 220° | <i>Wispek</i> , Ber. 16, 1577     |
| 2,3,5-Cumobenzyl alcohol,<br>$(\text{CH}_3)_3[2,4,5]\text{C}_6\text{H}_2[1]\text{CH}_2\text{OH}$     | 168°   | ..   | <i>Kraemer</i> , Ber. 24, 2411    |
| 3,4,5-Hemimellibenzy alcohol,<br>$(\text{CH}_3)_3[3,4,5]\text{C}_6\text{H}_2[1]\text{CH}_2\text{OH}$ | 78°    | ..   | <i>Kraemer</i> , Ber. 24, 2411    |
| <i>p</i> -Cumyl alcohol,<br>$(\text{CH}_3)_2\text{CH}[4]\text{C}_6\text{H}_4[1]\text{CH}_2\text{OH}$ | ..     | 249° | <i>Perkin</i> , J. 69, 1198       |
| Mellityl alcohol, $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}_2\text{OH}$                          | 160°   | ..   | <i>Jacobsen</i> , Ber. 22, 1217   |

Among other homologues may be mentioned: *Phenyl-ethyl alcohols*: **Benzyl carbinol**,  $\beta$ -phenyl-ethyl alcohol,  $\text{PhCH}_2\text{CH}_2\text{OH}$ , solidifying at  $-25.8^\circ$ , b.p.  $219^\circ$ , occurs in rose-oil and in other essential oils (*Soden*, Ber. 34, 2803). It is prepared: (1) from benzene, ethylene oxide, aluminium chloride and hydrochloric acid (*Smith, Natelson*, Am. 53, 3476); (2) from phenyl chloride, magnesium, and ethylene chlorhydrin or ethylene oxide, without the use of ether (*Schorigin*, Ber. 64, 2584); (3) from phenyl magnesium bromide and ethylene chlorhydrin (*Schlenck*, Ber. 64, 735); (4) by the action of ethylene chlorhydrin or ethylene oxide on phenyl sodium or potassium (Ger. Pats. 594,968 and 596,523). Its phenyl-urethane, m.p.  $80^\circ$ , diphenyl-urethane, m.p.  $99-100^\circ$ , hydrogen phthalic ester, m.p.  $188-189^\circ$ . It is dehydrated by potassium carbonate, giving styrene (p. 443) (*cf. Alder*, Ann. 501, 1).

**Phenyl-methyl carbinol**,  $\alpha$ -phenyl-ethyl alcohol,  $\text{PhCH}(\text{OH})\text{CH}_3$ , b.p.  $203^\circ$ , is obtained by the action of methyl magnesium iodide on benzaldehyde (*Grignard*, Ann. Lyon, 1901), and also by heating phenyl glycol with caustic potash (*Palfray*, C.r. 193, 941). Its phenyl-urethane, m.p.  $78^\circ$ , and that of phenyl-ethyl carbinol (p. 253) are used as soporifics (*Puyal*, Bull. 27, 857). When dehydrated by means of acids it gives styrene in addition to the ether (*Descamps*, Bull. Belg. 33, 139). It has been resolved into its optical antipodes; *d*-form,  $\alpha_D 42^\circ 88'$ , *l*-form,  $\alpha_D -10^\circ 94'$ ; the rotation is reversed in the halides (*Houssa, Kenyon*, J. 1930, 2260; 1931, 382).

**Tolyl-ethyl alcohol**,  $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH}$ , *o*-, m.p.  $243.5^\circ$ , *m*-, m.p.  $243^\circ$ , *p*-, m.p.  $245^\circ$ . These compounds are obtained by the action of ethylene chlorhydrin on tolyl-magnesium bromides (*Grignard*, Ann. chim. phys. [8], 10, 23), or by the electrolytic reduction of the three isomeric tolyl-acetic acids (*Kling*, C. 1908, II, 1863). *m*- and *p*-Tolyl-methyl and tolyl-ethyl carbinols,  $\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{OH})\text{Alk}$ , are obtained from the bromo-toluenes by the action of acetaldehyde or propionaldehyde, respectively, and magnesium (Ber. 55, 21). *p*-Tolyl-methyl carbinol has been detected in the oil of *Curcuma domestica* (Arch. Pharm. 27, 342).

**Phenyl-propyl alcohols**.—**Hydrocinnamyl alcohol**,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ , b.p.  $235^\circ$ , is obtained by catalytic or electrolytic reduction of cinnamaldehyde (*Skita*, Ber. 48, 1692; *Shima*, J. Kyoto, 1929). It occurs as the cinnamic ester in storax (*Miller*, Ann. 188, 202).  $\alpha$ -*n*-Amyldihydro-cinnamyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{C}_4\text{H}_9)\text{CH}_2\text{OH}$ , b.p.  $162^\circ$  (13 mm.) is obtained by the action of sodium benzyolate and *n*-amyl-cinnamaldehyde (p. 458) (*Palfray*, C.r. 203, 1523).  $\beta$ -Phenyl-butyl alcohol,  $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ , b.p.  $126-128^\circ$  (13 mm.) is obtained from  $\beta$ -methyl-hydrocinnamic ester (*Rupe*, Helv. 13, 361), and by the action of propionaldehyde on benzyl-magnesium bromide (*Lagerer*, Russ. 5, 515 (1935)).  $\beta$ , $\beta$ -Phenyl-methyl-propyl alcohol,  $(\text{CH}_3)_2\text{C}_6\text{H}_4\text{C}-\text{CH}_2\text{OH}$ , is obtained from benzyl cyanide as follows: Dimethyl benzyl cyanide is prepared, it is hydrolysed,

the acid obtained is converted into its isoamyl ester, and this ester is reduced with sodium and isoamyl alcohol (*Darzens*, C.r. 189, 1287).  $\beta$ -(*p*-Isopropyl-phenyl)-ethyl alcohol,  $C_6H_7[4]C_6H_4[1]CH_2CH_2OH$ , b.p.  $154^\circ$  (28 mm.), is obtained from *p*-cumyl-magnesium bromide, and trihydroxy-methylene (*Bert*, Bull. 37, 1397).

**Benzyl-methyl carbinol**,  $C_6H_5CH_2CH(OH)CH_3$ , *d,l*-form, b.p.  $215^\circ$ ; *l*-form,  $\alpha_{D_{40}}^{20} -32.18^\circ$ ; *d*-form, b.p.  $125^\circ$  (25 mm.),  $\alpha_{D_{40}}^{20} +33.02^\circ$ ; acetic ester of the *d*-form, b.p.  $115^\circ$  (10 mm.),  $\alpha_{D_{40}}^{20} +7.13^\circ$ , hydrolyses into the unchanged carbinol, and esters with other carboxylic acids behave in the same way. On the other hand, the *p*-toluene-sulphonic ester of the *d*-form, m.p.  $94^\circ$ ,  $\alpha_{D_{40}}^{20} +31.11^\circ$  in benzene, gives with potassium acetate, the acetic ester of the *l*-form,  $\alpha_{D_{40}}^{20} -7.06^\circ$ , hydrolysing to the *l*-carbinol. It is inferred that on hydrolysis of the carboxylic esters, the carboxyl and alkoxyl groups separate, but on hydrolysis of alkyl sulphonates the anionic group,  $RSO_3^-$ , leaves the alkyl carbon, with a Walden inversion at the asymmetric alkyl carbon (*Kenyon*, J. 105, 2262; *Phillips*, J. 123, 44).

**Phenyl-ethyl carbinol**,  $PhCH(OH)C_2H_5$ , b.p.  $221^\circ$ , has been resolved by *Pickard* and *Kenyon*, J. 99, 45. This alcohol, and phenyl-propyl, phenyl-isopropyl, phenyl-isobutyl, and phenyl-isoamyl carbinols, b.p.  $114^\circ$  (10 mm.), b.p.  $113^\circ$  (15 mm.), (m.p.  $16^\circ$ ), b.p.  $122^\circ$  (6 mm.), and b.p.  $132^\circ$  (8 mm.), respectively, are prepared from benzaldehyde and the respective alkyl-magnesium iodides (C. 1910, II, 623) (method 9b). **Phenyl-tert.-amyl carbinol**, b.p.  $125^\circ$  (12 mm.), is obtained from the ketone (p. 284) by reduction (*Favorski*, Russ. 5, 1679).  $\beta$ -Phenyl-isobutyl-methyl carbinol,  $(CH_3)_2C_6H_4C(CH_3)CH_2CH(OH)CH_3$ , b.p.  $132-133^\circ$  (17 mm.), is obtained from the ketone (*Hoffman*, Am. 51, 2542). **Phenyl-dimethyl carbinol**,  $C_6H_5C(OH)(CH_3)_2$ , m.p.  $23^\circ$ , b.p.  $94^\circ$  (10 mm.), is obtained by the action of acetone on phenyl magnesium bromide, or by the action of magnesium methyl iodide on acetophenone, or methyl benzoate. **Phenyl-methyl-butyl carbinol**,  $(CH_3)(C_4H_9)C(C_6H_5)C^*OH$ , b.p.  $129-130^\circ$  (12 mm.), is obtained by the action of butyl magnesium bromide on acetophenone (*Conant*, Am. 54, 4048). **Phenyl-methyl-n-nonyl carbinol**,  $(CH_3)(C_9H_{19})(C_6H_5)C^*OH$ , b.p.  $200-203^\circ$  (14 mm.), is obtained from methyl-nonyl ketone and phenyl magnesium bromide. It is a viscous oil with a smell of nasturtium leaves (*Ar. Pharm.* 263, 264). **Benzyl-dimethyl carbinol**,  $C_6H_5CH_2C(OH)(CH_3)_2$ , m.p.  $24^\circ$ , b.p.  $225^\circ$ , has a lilac odour. Other dialkyl-phenyl- and dialkyl-benzyl carbinols are described by *Kononov* and *Conant* (Am. 54, 4048).

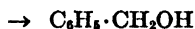
### Functional Derivatives of Phenyl Paraffin Alcohols

**Halides**.—Benzyl chloride and bromide are produced by the action of chlorine or bromine on boiling toluene (p. 54) (*Beilstein*, Ann. 143, 369). The reaction is accelerated by sunlight (C. 1898, I, 1019). Nitrosyl chloride at  $150^\circ$  acts similarly (*Quist*, C.r. 198, 1424). Benzyl fluoride is obtained by thermal decomposition of trimethyl-benzyl-ammonium fluoride, and the chloride, bromide, and iodide are also obtained by the action of the hydrogen halides or benzyl alcohol. The chloride and bromide may be obtained from benzene and dichloro- or dibromo-methyl ether in the presence of zinc chloride, and the iodide by the action of potassium iodide on the chloride (*Rumpf*, Ann. 224, 126).

|                                       | M.p.         | B.p.          |                             |
|---------------------------------------|--------------|---------------|-----------------------------|
| Benzyl fluoride, $C_6H_5CH_2F$ .....  | $-35^\circ$  | $139.9^\circ$ | } powerful<br>lachrymators. |
| Benzyl chloride, $C_6H_5CH_2Cl$ ..... | $-39^\circ$  | $176^\circ$   |                             |
| Benzyl bromide, $C_6H_5CH_2Br$ .....  | $-3.9^\circ$ | $210^\circ$   |                             |
| Benzyl iodide, $C_6H_5CH_2I$ .....    | $24^\circ$   | Dec.          |                             |

Benzyl chloride, isomeric with the three chloro-toluenes, is an important reagent, as numerous derivatives of benzyl alcohol can be prepared from it. Its chlorine atom is readily replaced. It gives

benzyl alcohol when boiled with water, and when heated with water and lead nitrate it gives benzaldehyde and benzoic acid:



**HOMOLOGOUS PHENYL-ALKYL CHLORIDES.**  $\alpha$ -Chloro-ethyl-benzene,  $\text{C}_6\text{H}_5\text{CHCl}\cdot\text{CH}_3$ , b.p.  $194^\circ$  (Fischer, Ber. 39, 2209; Blanc, Bull. 33, 313).  $\beta$ -Chloro-ethyl-benzene, phenyl-ethyl chloride, b.p.  $96^\circ$  (23 mm.), is obtained by the action of hydrogen chloride on  $\beta$ -phenyl-ethyl alcohol (Ferser, Ber. 62, 183). Phenyl-ethyl bromide, b.p.  $77\text{--}80^\circ$  (3 mm.) (Horne, Shriner, Am. 55, 4652). Methyl-benzyl chloride, *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ , b.p.  $198^\circ$ ,  $195^\circ$ , and  $192^\circ$ , respectively. Cumyl chloride,  $\text{C}_6\text{H}_7[4]\text{C}_6\text{H}_4[1]\text{CH}_2\text{Cl}$ , b.p.  $100^\circ$  (14 mm.), is obtained from cumene, trihydroxymethylene, anhydrous zinc chloride, and hydrogen chloride gas (Blanc, Bull. 33, 313).  $\alpha$ -Chloro-propyl-benzene,  $\text{C}_6\text{H}_5\text{CHCl}\cdot\text{CH}_2\cdot\text{CH}_3$ , and  $\beta$ -chloro-propyl-benzene,  $\text{C}_6\text{H}_5\text{CH}_2\text{CHClCH}_3$ , boil about  $203\text{--}207^\circ$ , losing hydrogen chloride and forming  $\alpha$ -phenyl-propylene,  $\text{Ph}\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$ , and allyl-benzene,  $\text{Ph}\cdot\text{CH}_2\text{CH}:\text{CH}_2$ .  $\omega$ -Bromo-propyl-benzene,  $\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , b.p.  $109^\circ$  (11 mm.) (Rupe, Ber. 43, 178). For  $\omega$ -chloro-alkyl-benzenes ( $\omega$ -phenyl-alkyl chlorides) see Braun, Ber. 44, 2867, and Kohn, Mo. 44, 197. *p*-Bromo-benzyl chloride, m.p.  $40^\circ$ , is obtained from phenyl bromide, trihydroxymethylene and stannic chloride saturated with hydrogen chloride (Quelet, Bull. 41, 329). Nitro-benzyl halides (p. 261; Moureu, Bull. 29, 1006; Pogg, Lincei [6], 2, 423) are used for identifying organic acids as their nitrobenzyl esters (Lynn, Am. 39, 701).

Ethers of benzyl alcohol are obtained from benzyl chloride by the action of sodium alkylates, or by electrolytic reduction of benzoic esters (Mettler, Ber. 38, 1752). Catalytic reduction may also be used (Senderens, C.r. 178, 1412). When the benzyl ethers are heated with caustic alkalis, they partly rearrange, giving carbinols,  $\text{C}_6\text{H}_5\text{CHOH}\cdot\text{Alk}$  (Schorigin, Ber. 57, 1634). Benzyl-methyl ether, b.p.  $168^\circ$ , is also obtained by the action of phenyl magnesium bromide on monochloro-methyl ether (Reychler, Bull. 1, 1195). Benzyl-chloromethyl ether,  $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{Cl}$ , b.p.  $103^\circ$  (13 mm.), is obtained from benzyl alcohol, formaldehyde and hydrogen chloride (Carré, C.r. 186, 1629). Mixed acetals of formaldehyde with aliphatic and aryl-aliphatic residues,  $\text{Alk}\cdot\text{OCH}_2\cdot\text{OCH}_2\text{Ar}$ , are formed by the interaction of chloromethyl alcohols,  $\text{Alk}\cdot\text{OCH}_2\text{Cl}$ , and the sodium compounds of aromatic alcohols (Schmied, Ber. 1929, 201). Benzyl-ethyl ether, b.p.  $185^\circ$ . Benzyl-monoglycol ether,  $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ , b.p.  $132\text{--}135^\circ$  (13 mm.) obtained by the action of sodium benzyolate on glycol chlorhydrin, is an analgesic and anesthetic (U. S. Pat. 1,651,458). Methylene-dibenzyl ether,  $\text{CH}_2(\text{OCH}_2\text{C}_6\text{H}_5)_2$  (Arnhold, Ann. 240, 200). Benzyl arabinoside,  $\text{C}_6\text{H}_5\text{O}_5\text{CH}_2\text{C}_6\text{H}_5$ , m.p.  $172^\circ$  (Fischer, Ber. 27, 2482). Benzyl-phenyl ether, m.p.  $39^\circ$ , b.p.  $287^\circ$ , is converted into *o*- and *p*-benzyl-phenol, and *o,p*-dibenzyl-phenol, when digested with zinc or copper at  $250^\circ$  (Behaghel, Ber. 67, 1368). For benzyl ethers of phenols and the isomeric *o*-benzyl-phenols, see Claisen, Ann. 442, 237. Benzyl ether,  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{O}$ , b.p.  $296^\circ$ , dipole moment 1.38 D., is obtained by the action of sulphuric acid or boric acid on benzyl alcohol (Lowe, Ann. 241, 374; Meissenheimer, Ber. 41, 1421). Phenyl-ethyl-*n*-propyl ether, b.p.  $225\text{--}227^\circ$ , is obtained by reduction of the di-*n*-propyl acetal of phenylacetaldehyde (Sigmund, Mo. 48, 267).

**Esters of inorganic acids.**—Benzyl phosphates: the mono-phosphate melts at  $78^\circ$ , the di-phosphate is a liquid, and the tri-phosphate melts at  $64^\circ$  (Lossen, Ann. 262, 211). Benzyl-sulphuric acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{OSO}_3\text{H}$ , is formed, together with dibenzyl formal,  $\text{CH}_2(\text{OCH}_2\text{C}_6\text{H}_5)_2$ , by the action of methylene sulphate,  $\text{SO}_4\cdot\text{CH}_2$ , on benzyl alcohol (Delepine, C.r. 129, 831; Bull. [3], 21, 1059). Benzyl nitrite,  $\text{C}_6\text{H}_5\text{CH}_2\text{ONO}$ , b.p.  $81^\circ$  (35 mm.) is obtained by the action of nitrous acid on benzyl alcohol in aqueous solution (Raeyer, Ber. 34, 755).

Carboxylic esters can be prepared by esterifying alcohols or chlorides directly, or by means of aluminium alkylates. Thus, a mixture of benzyl alcohol, methyl salicylate and aluminium benzyolate yields benzyl salicylate. Esters of the lower fatty acids have characteristic odours.

Benzyl acetate,  $\text{PhCH}_2\text{OCOCH}_3$ , b.p.  $216^\circ$ , occurs in oil of jasmine. Benzyl valerate is used to counter convulsions (Kubig, C. 1924, I, 1691). Sodium reacts

in a curious manner with the benzyl esters of fatty acids, converting them into benzyl esters of higher phenyl-fatty acids (p. 293). Thus, benzyl acetate gives benzyl phenyl-propionate. **Dibenzyl oxalate**,  $(C_6H_5CH_2OCO)_2$ , m.p.  $80^\circ$ .

**Benzyl chloroformate**,  $C_6H_5CH_2OCOCl$ , obtained by the action of phosgene on benzyl alcohol, is used in the synthesis of peptides for the introduction of the  $C_6H_5CH_2O \cdot CO$  residue into the amino-group of amino-acids. The carbo-benzyloxy residue is readily eliminated as toluene and carbon dioxide by mild catalytic hydrogenation, and the peptide linkage remains intact (*Bergmann, Ber. 65, 1192*).

### *Sulphur Derivatives of Benzyl Alcohol*

These compounds are formed in an exactly similar manner to their aliphatic analogues.

**Benzyl hydrosulphide**, *benzyl mercaptan*,  $C_6H_5CH_2SH$ , b.p.  $194^\circ$ ,  $d_{16} 1.058$ , is a liquid with an odour of leeks (*Märker, Ann. 140, 86*). In addition to the usual methods, it can be obtained by acting upon benzyl chloride with sodium thiosulphate, when sodium benzyl-thiosulphate is produced, and decomposing the latter with sulphuric acid, when benzyl mercaptan and benzyl disulphide are formed (*Fr. Pat. 667,551*).

**Benzyl sulphide**,  $(C_6H_5CH_2)_2S$ , m.p.  $49^\circ$ , occurs also in a liquid modification (*Hinsberg, Ber. 62, 127; 64, 2500*). **Benzyl disulphide**,  $(C_6H_5CH_2)_2S_2$ , m.p.  $71^\circ$  (*Hofmann, Ber. 20, 15*), is formed simply by exposing benzyl hydrosulphide to air (*Märker, Ann. 136, 86*) and can be prepared by electrolysis of sodium benzyl-hyposulphite, or treating it with iodine (*Price, J. 91, 2021; 95, 1489*). These compounds decompose on heating, forming stilbene,  $C_6H_5CH:CHC_6H_5$ , sulphur, and hydrogen sulphide as primary products; secondary reactions occur, giving rise to toluene, tetraphenyl-thiophene, and tetraphenyl-butane. Dibenzyl sulphoxide and dibenzyl sulphone yield similar products (*Fromm, Ber. 36, 534*).

**Benzyl-dimethyl-sulphine iodide**,  $C_6H_5CH_2S(CH_3)_2I$ , is an orange coloured compound (*Schüller, Ber. 7, 1274*). **Tribenzyl-sulphine chloride**,  $(C_6H_5CH_2)_3S \cdot Cl$ . The double salt of this compound with ferric chloride occurs as light-green flakes, m.p.  $98^\circ$ , and is obtained by the action of ferric chloride on an ether solution of benzyl chloride and benzyl sulphide. **Tribenzyl-sulphine iodide**, m.p.  $75^\circ$  (*Hofmann, Ber. 40, 4932*).

**Benzyl sulphoxide**,  $(C_6H_5CH_2)_2SO$ , m.p.  $133^\circ$ , is formed by oxidising benzyl sulphide or hydrosulphide with nitric acid or hydrogen peroxide (*Otto, Ber. 13, 1284*). **Benzyl sulphone**,  $(C_6H_5CH_2)_2SO_2$ , m.p.  $150^\circ$ , is obtained by oxidising benzyl sulphoxide with potassium permanganate in glacial acetic acid (*Otto, loc. cit.*). **Benzyl disulphoxide**,  $C_6H_5CH_2SOSOCH_2C_6H_5$ , m.p.  $108^\circ$ , is obtained by the action of hydrogen peroxide on benzyl disulphide or hydrosulphide. Both sulphoxides are also found among the products of electrolytic oxidation of benzyl disulphide (*Fichter, Ber. 43, 3422*).

**Methyl- and ethyl-benzyl sulphones**, m.p.  $127^\circ$  and  $84^\circ$ , respectively, are obtained from sodium benzyl-sulphinate and methyl iodide and ethyl iodide, respectively. **Benzyl-sulphinic acid**,  $C_6H_5CH_2SO_2H$ , produced by reducing benzyl sulphochloride, decomposes readily into benzaldehyde and sulphur dioxide (*Fromm, Ber. 39, 3308, 3315*). **Benzyl-sulphonic acid**,  $C_6H_5CH_2SO_3H$ , a deliquescent crystalline substance, is isomeric with the toluene-sulphonic acids. Its potassium salt is obtained by boiling benzyl chloride with potassium sulphite. Chloride, m.p.  $92^\circ$  (*Otto, Ber. 13, 1289*). Hydrazide, m.p.  $131-132^\circ$  (decomp.); azide, m.p.  $54^\circ$  (*Curtius, J. pr. 102, 85*). Nitro- and amino-benzyl-sulphonic acids, and benzyl hyposulphurous acid,  $C_6H_5CH_2SSO_3H$ , m.p.  $74^\circ$  (*Purgotti, Gazz. 20, 24*).

**Benzyl-xanthogenic methyl and ethyl esters**,  $C_6H_5CH_2CSS \cdot OAlk$ , m.p.  $29^\circ$  and b.p.  $170-171^\circ$  (14 mm.), respectively, are obtained from benzyl alcohol, sodium, and carbon disulphide, and alkylating with dialkyl sulphate (*Nametkin, J. pr. 112, 164*).

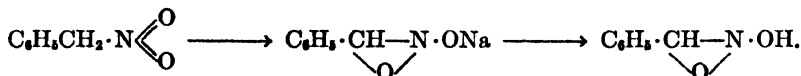
**METALLO-BENZYL COMPOUNDS.** Lithium benzyl,  $C_6H_5CH_2Li$ , has been prepared, in solution only, by the action of benzyl magnesium chloride on lithium-phenyl (*Ziegler, Ann. 479, 178*).



*Nitrogen Derivatives of Phenyl Paraffin Alcohols*

**PHENYL NITRO-PARAFFINS.** When the homologues of benzene are heated with dilute nitric acid in sealed tubes, the nitro-groups usually enter the side-chains only, and phenyl nitro-paraffins are formed (*Konovalov*, Ber. 28, 1850; 29, 2199). Thus, toluene gives phenyl nitromethane,  $C_6H_5 \cdot CH_2NO_2$ , an oil, b.p.  $142^\circ$  (35 mm.). This can also be prepared from nitro-benzylidene phthalide, or from benzyl halides, preferably the iodide, by the action of silver nitrite (*Hantzsch*, Ber. 29, 700), or by the action of mercurous nitrite on the chloride (*Neogi*, Z. anorg. Chem. 69, 270). It is most easily obtained from pheno-nitro-acetonitrile,  $C_6H_5CH(NO_2)CN$  (*q.v.*), by boiling with sodium hydroxide, or by the action of ethyl nitrate and potassium ethylate on phenylacetic ester, a reaction in which the carbethoxy group of the phenyl-nitro-acetate,  $C_6H_5CH(NO_2) \cdot COOC_2H_5$ , first formed, is split off in the form of ethyl carbonate. Phenyl-nitromethane is decomposed on heating with sodium hydroxide at  $160^\circ$ , oxides of nitrogen being liberated and stilbene formed (*Wislicenus*, Ber. 36, 1194; 38, 502; 42, 1930). For its behaviour on distillation with steam, see *Heim*, Ber. 43, 3417.

Phenyl-nitromethane dissolves in aqueous sodium hydroxide in the same way as the nitroparaffins (Vol. I, p. 178), with the formation of a sodium salt. The action of carbon dioxide or acetic acid on the sodium salt re-forms the phenyl-nitromethane as an oil, but if the solution of the sodium salt is precipitated by the addition of a mineral acid, a crystalline substance, m.p.  $84^\circ$ , is obtained. The latter is the isomeric *aci*-form of common phenyl nitromethane, and is distinguished from it by giving a red colour with ferric chloride, and by being a conductor of electricity. It rapidly changes to the oily isomer both in solution and in the solid state. It probably has the structure which has already been put forward for the sodium salts of the nitroparaffins. In the case of the aliphatic series, however, most of the corresponding free nitro-compounds are unknown:



Similar stable and unstable forms of ring-homologues, and of substitution products of phenyl-nitromethane are known (*Konovalov*, Ber. 29, 2193; *Hantzsch*, Ber. 29, 2251; *Holleman*, Rec. 14, 121).

When acid chlorides act upon the sodium salts of phenyl-nitromethanes, an internal molecular oxidation takes place, and acyl derivatives of benzhydroxamic acid are formed. Thus *acetyl-benzhydroxamic acid*,  $C_6H_5C(OCOCH_3)NOH$ , is formed by the action of acetyl chloride on sodio-phenyl-nitromethane (*Thiele*, Ann. 309, 189). For ammonium salts of phenyl-nitromethane, see *Bamberger*, Ber. 33, 1781.

**TOLYL-NITROMETHANES**, see *Wislicenus*, Ber. 38, 503; *Konovalov*, C. 1905, II, 817.  $\omega$ -Nitrodurene,  $(CH_3)_2[2,4,5]C_6H_2[1]CH_2NO_2$ , m.p.  $52^\circ$ , isonitro-compound, m.p.  $102-106^\circ$ , is readily obtained by nitrating durene with benzoyl nitrate (*Willstätter*, Ber. 42, 4154).

Phenyl-methyl-nitromethane,  $C_6H_5CH(CH_3)NO_2$ , b.p.  $115^\circ$  (11 mm.), is obtained by oxidation of acetophenone-monoxime with permonosulphuric acid. Its highly unstable *aci*-form,  $C_6H_5C(CH_3):NOOH$ , melts about  $45^\circ$  (*Bamberger*, Ber. 36, 706). *o*-, *m*-, *p*-Nitrophenyl-nitromethane, m.p.  $72^\circ$ ,  $94^\circ$ ,  $91^\circ$ , respectively.

**PHENYL PARAFFIN AMINES, BENZYLAMINES.** (1) *Mono*-, *di*- and *tri*-benzylamines are formed by the action of alcoholic ammonia on benzyl chloride (*Liebig*, Ber. 23, 2971; *Duhomme*, C.r. 193, 636). This method, together with most of the others available for the preparation of benzylamine have been described in the section on primary alkylamines. Benzylamine is obtained: (2) by the reduction of phenyl-nitromethane, benzaldoxime, and benzylidene-phenyl-hydrazone (*Tafel*, Ber. 19, 1928; 35, 1513; *Paal*, Ber. 42, 1559); (3) and (4) by heating benzaldehyde with ammonium formate or

formamide (*Linckardt*, Ber. 19, 2128; 20, 184; *Wallach*, Ann. 343, 54). Di- and tri-benzylamine are also produced in this reaction; by the reduction of (5) benzonitrile (*Paal*, Ber. 42, 1554; Fr. Pat. 638,550), (6) of benzothiamide (*Bamberger*, Ber. 21, 51) and (7) benzamide (Ger. Pat. 396,453); by hydrolysis of (8) benzyl isocyanate,  $C_6H_5CH_2NCO$  (*Strakosch*, Ber. 5, 682), and (9) benzyl-acetamide,  $C_6H_5CH_2CHCOCH_3$  (Ber. 59, 2663); (10) by distillation of phenyl-aminoacetic acid,  $C_6H_5CH(NH_2)COOH$  (*Tiemann*, Ber. 14, 1969); (11) from phenyl-acetamide by the action of bromine and caustic soda; and (12) by the action of monochloroamine on benzyl magnesium chloride (*Coleman*, Am. 50, 1193).

**Benzylamine**,  $C_6H_5CH_2NH_2$ , b.p.  $184^\circ$ , a liquid, freely soluble in water, is a much stronger base than the toluidines, with which it is isomeric, and combines with carbon dioxide from the air.

It is oxidised by permonosulphuric acid to benzaldoxime, phenyl-nitromethane, benzhydroxamic acid, benzaldehyde, and benzoic acid (*Bamberger*, Ber. 34, 2262).

**Methyl-benzylamine**, b.p.  $78^\circ$  (14 mm.), is an oil. It occurs in the Chinese drug *ma-huang* (*Ephedra vulgaris*). Its hydrochloride melts at  $180.5^\circ$  (*Ling Chen*, Am. Pharm., 20, 339). It is obtained from benzaldehyde and methylamine by hydrogenation. **Diethyl-benzylamine** is obtained in a similar manner using diethylamine. It boils at  $94^\circ$  (15 mm.) (*Wegler*, Ber. 69, 2071).

**Dibenzylamine**,  $(C_6H_5CH_2)_2NH$ , b.p.  $186^\circ$  (19 mm.), is obtained from benzalazine,  $C_6H_5CH:N:N:CHC_6H_5$ , by reduction with zinc dust and acetic acid. It is also formed, together with benzylamine, by reduction of benzonitrile; nitroso-dibenzylamine,  $(C_6H_5CH_2)_2NNO$ , m.p.  $61^\circ$  (*Curtius*, Ber. 34, 557). **Tribenzylamine**,  $(C_6H_5CH_2)_3N$ , m.p.  $92^\circ$ , is obtained by the action of sodamide on benzyl chloride (*Wegler*, Ber. 69, 2071).

**HOMOLOGUES OF BENZYLAMINE** are isomeric with the corresponding arylamines (p. 78). They are usually obtained by reducing nitriles with alcohol and sodium, and sometimes by electrolytic reduction of oximes or nitro-compounds or by other methods mentioned under benzylamine.

$\beta$ -Phenyl-ethylamine,  $C_6H_5CH_2CH_2NH_2$ , b.p.  $19.7^\circ$  (*Bischler*, Ber. 26, 1904).

$d,l$ - $\alpha$ -Phenyl-ethylamine,  $C_6H_5CH(NH_2)CH_3$ , b.p.  $187^\circ$  (*Kann*, Ber. 27, 2306).

$\gamma$ -Phenyl-propylamine,  $C_6H_5CH_2CH_2CH_2NH_2$ , b.p.  $221^\circ$  (*Senfter*, Ber. 27, 2309).

$\beta$ -Phenyl-propylamine,  $C_6H_5CH(CH_3)CH_2NH_2$ , b.p.  $210^\circ$  (*Freund*, Ber. 26, 2875).

$\alpha$ -Phenyl-propylamine,  $C_6H_5CH(NH_2)CH_2CH_3$ , b.p.  $205^\circ$ .

$\beta$ -Phenyl-isopropylamine,  $C_6H_5CH_2CH(NH_2)CH_3$ , b.p.  $203^\circ$  (*Edeleano*, Ber. 20, 618).

*o*-Tolubenzylamine,  $CH_3[2]C_6H_4[1]CH_2NH_2$ , b.p.  $205^\circ$  (*Bamberger*, Ber. 23, 1026; 33, 113).

*m*-Tolubenzylamine,  $CH_3[3]C_6H_4[1]CH_2NH_2$ , b.p.  $205^\circ$  (*Curtius*, J. pr. 62, 113).

*p*-Tolubenzylamine,  $CH_3[4]C_6H_4[1]CH_2NH_2$ , b.p.  $204^\circ$  (*Curtius*, loc. cit.).

$\omega$ -Pseudocumylamine,  $(CH_3)_2CH[2,4]C_6H_3[1]CH_2NH_2$ , m.p.  $28.5^\circ$  (*Curtius*, loc. cit.).

$\alpha$ -(*p*-Tolyl)-ethylamine,  $CH_3[4]C_6H_4[1]CH(CH_3)NH_2$ , b.p.  $207^\circ$  (*Kindler*, Ber. 68, 2241).

$\omega$ -Mesitylamine,  $(CH_3)_3[3,5]C_6H_3[1]CH_2NH_2$ , b.p.  $221^\circ$  (*Kononov*, C. 1899, I, 1238).

$\omega$ -Durylamine (2 forms),  $(CH_3)_3[2,4,5]C_6H_2[1]CH_2NH_2$ , m.p.  $52^\circ$  and  $64^\circ$  (*Willstätter*, Ber. 42, 4156; *Kraemer*, Ber. 24, 2409).

Cumylamine,  $(CH_3)_3CH[4]C_6H_4[1]CH_2NH_2$ , b.p.  $1226^\circ$  (*Goldschmidt*, Ber. 20, 2414).

Hemimellibenzyllamine,  $(CH_3)_3[3,4,5]C_6H_2[1]CH_2NH_2$ , m.p.  $123^\circ$  (*Kroemer*, Ber. 24, 2411).

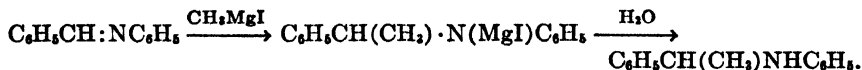
**$\alpha$ -Phenyl-ethylamine**,  $C_6H_5CH(NH_2)CH_3$ , can be obtained from ethyl hydrocinnamate by Curtius' method, the hydrazide being prepared, and this acted upon by sodium nitrite (*Saha*, Rep. Tsing Hua, 3, 525). It can also be obtained by electrolytic reduction of acetophenone oxime (*Tafel*, Ber. 35, 1515). It contains an asymmetric carbon atom, and has been resolved by means of the malate (*Pope*, Proc. 15, 200; *Loven*, J. pr. 72, 307).  **$\beta$ -Phenyl-ethylamine** has been prepared by reducing  $\omega$ -nitrostyrene, by condensing benzyl bromide with hexamethylene tetramine, and hydrolysing the product, and by the action of hot sodium hydroxide on hydrocinnamyl-N-chloro-amide (Ger. Pat. 562,714). It is a local anaesthetic. For its action on the heart see *Barbour*, J. Pharm. Ther. 1915. For acyl- $\beta$ -phenyl-ethylamines see *Decker*, Ann. 395, 282. The isomeric phenylpropylamines also increase blood pressure (*Hartung*, Am. 53, 1875; *Alles*, Am. 54, 271).

Benzyl-alkyl- and benzyl-aryl-amines, and benzyl-alkyl-ammonium compounds are derived from the simple benzylamines. The benzyl-alkylamines, such as **benzyl-ethylamine**,  $C_6H_5CH_2NHC_2H_5$ , and  **$\alpha$ -cumyl-ethylamine**,  $C_6H_5C_6H_4CH_2NHC_2H_5$ , are obtained from the corresponding benzylidene-alkylamines (p. 272) by reduction with sodium and ethyl alcohol, or by heating benzaldehyde with formates of organic bases (*Schwabbauer*, Ber. 35, 410; *Wallach*, Ann. 343, 54).

**$\beta$ -Phenylethyl-methylamine**,  $C_6H_5CH_2CH_2NHC_2H_5$ , b.p. 205°, is prepared by condensing phenylacetaldehyde and methylamine in the presence of sodium hydroxide, and reducing the condensation product with sodium and alcohol (*Barger*, J. 97, 2253). **Dibenzyl-ethylene diamine**,  $(C_6H_5CH_2NH)_2C_2H_4$ , b.p. 222° (18 mm.), obtained from dibenzylidene-ethylene diamine, condenses with ethylene bromide to *dibenzyl-piperazine*. **Phenylpropyl-methylamine**,  $C_6H_5CH_2CH_2CH_2NHC_2H_5$ , b.p. 134° (18 mm.), is obtained from cinnamylidene-methylamine,  $C_6H_5CH:CH:CH:NCH_3$ , by reduction with sodium and alcohol (*Schwabbauer*, Ber. 35, 410).  **$\alpha$ -Phenylethyl-methylamine**,  $C_6H_5(CH_2)CHNHC_2H_5$ , b.p. 87° (18 mm.), and  **$\alpha$ -phenylpropyl-methylamine**, b.p. 96° (20 mm.), are formed by the interaction of benzylidene-methylamine,  $C_6H_5CH:NMe$ , and methyl magnesium iodide or ethyl magnesium iodide, respectively (*Busch*, J. pr. 77, 20).

**Benzyl-phenyl-allyl-methyl-ammonium iodide**,  $(C_6H_5CH_2)(C_6H_5)(C_6H_5)(CH_2)NI$ , contains an asymmetric nitrogen atom, and has been resolved by means of camphor sulphonic acid (*Wedekind*, Ber. 32, 3561; *Græbe*, Ber. 34, 1778). Many other quaternary benzyl-ammonium compounds with four different radicals have also been resolved (p. 82).

**N-Benzyl-aniline**,  $C_6H_5CH_2NHC_6H_5$ , m.p. 36°, is obtained by the action of benzyl chloride or benzyl alcohol on aniline (*Knoevenagel*, J. pr. 89, 32; *Wilson*, Org. Synth. 8, 38), or by reduction of benzylidene aniline,  $C_6H_5CH:NHC_6H_5$ , with sodium and alcohol, or electrolytically (*Brand*, Ber. 42, 3460). When heated with sulphur, it forms *thiobenzanilide* at 220°, and *benzyl-amino-thiophenol*, at 250° (*Wallach*, Ann. 259, 300). Acid derivatives: **Dibenzylaniline**,  $(PhCH_2)_2NPh$ , m.p. 67° (*Matzudaira*, Ber. 20, 1611). **C-Alkyl-benzylanilines**, such as  $PhCH(Me)NPh$ , are obtained by addition of alkyl magnesium halides to benzylidene aniline (p. 272):



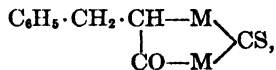
When the hydrochlorides of these bases are heated at 220° with aniline hydrochloride, they undergo an atomic migration, similar to the Hofmann rearrangement (p. 73), C-alkyl-*p*-amino-diphenylmethanes being formed, e.g.,



**C-Methyl-, -ethyl-, -propyl-, and amyl-benzyl-aniline**, b.p. 183° (20 mm.), 192°, 200°, and 215° (*Busch*, Ber. 38, 1761).

**Benzyl-oxethylamine**,  $Ph \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2OH$ , *picrate* m.p. 136°, is formed by the rupture of the phenyl-oxazoline ring,  $C_6H_5 \cdot C \begin{array}{l} \diagup O-CH_2 \\ \diagdown N-CH_2 \end{array}$ , (Vol. IV) by sodium and alcohol (*Gabriel*, Ber. 29, 2382).

The following representatives of the numerous class of benzylated acid amides and benzylated nitrogen derivatives of carbonic acid may be mentioned: **Benzyl-acetamide**,  $\text{PhCH}_2\text{NHCOCH}_3$ , m.p.  $60^\circ$  (*Amsel*, Ber. 19, 1286). Its nitroso-derivative,  $\text{PhCH}_2\text{N(NO)COCH}_3$ , is decomposed by alcohols with elimination of nitrogen, and formation of *benzyl-alkyl ethers* (p. 254). This decomposition, which recalls the diazonium compounds (p. 122), is also shown by other nitroso-acid derivatives of benzylamine (*Pechmann*, Ber. 31, 2640; *Paal*, Ber. 32, 78). **Dibenzyl-urea chloride**,  $(\text{PhCH}_2)_2\text{NCOCl}$ , is an oil (*Hammerich*, Ber. 25, 1819). **Benzyl-urethane**,  $\text{PhCH}_2\text{NHCOOC}_2\text{H}_5$ , m.p.  $44^\circ$ . **Benzyl-urea**,  $\text{PhCH}_2\text{NHCONH}_2$ , m.p.  $147^\circ$ . *Sym*- and *as*-dibenzyl-urea, melt at  $167^\circ$  and  $124^\circ$  respectively (*Schiff*, Ber. 9, 81). Tri- and tetra-benzyl-urea melt at  $119^\circ$  and  $85^\circ$  respectively (*Hammerich*, Ber. 25, 1826). **Benzyl-thiourea**, m.p.  $164^\circ$  (*Salkowski*, Ber. 24, 2727; *Hecht*, Ber. 25, 817). **Dibenzyl-guanidine**,  $(\text{PhCH}_2\text{NH})_2\text{C:NH}$ , m.p.  $100^\circ$  (*Strakosch*, Ber. 5, 695). **Benzyl-isocyanate**,  $\text{PhCH}_2\text{N:CO}$ , is a liquid with a penetrating odour (*Hadley*, Am. 34, 923). **Benzyl cyanurate** m.p.  $157^\circ$ . **Benzyl-mustard oil**,  $\text{PhCH}_2\text{N:CS}$ , b.p.  $243^\circ$ , is the chief ingredient of the essential oils of various cresses, where it is present as a glucoside (*Backer*, Rec. 54, 57). Homologous mustard oils have been obtained by a somewhat tedious method from dithiocarbamates, which, on treatment with iodine, give thiuram disulphides. These, when treated with sodium ethylate and iodine, give cyclic disulphides (*Braun*, Ber. 45, 2188; *Schneider*, Ber. 47, 1248, 2218). **Phenyl-ethyl-mustard oil**, b.p.  $141\text{--}144^\circ$  (11 mm.), occurs in water-cress oil, mignonette root oil, and other oils, and possibly in the oil extracted from mignonette flowers (*Schimmel's Berichte* 1929, 121). **Benzyl-thiohydantoin**,



m.p.  $185^\circ$ , is obtained by reduction of benzylidene-thiohydantoin (*Johnson*, J. Biol. Ch. 12, 205). **Phenyl-propyl-mustard oil**, b.p.  $163\text{--}166^\circ$ , occurs in minute quantities in horse-radish oil (*Heiduschka*, J. pr. 132, 201).

**BENZYL-HYDRAZINES**. **Benzyl-hydrazine**,  $\text{PhCH}_2\text{NH}\cdot\text{NH}_2$ , b.p.  $103^\circ$  (41 mm.), is obtained by the action of acids on the benzylidene compound  $\text{PhCH}_2\text{N:N:CHPh}$ , which is itself the product of partial reduction of benzylidene-azine (p. 273) with sodium amalgam and alcohol. Benzyl-hydrazine gives a very stable nitroso-compound,  $\text{PhCH}_2\text{CH}_2\text{N(NO)NH}_2$ , m.p.  $71^\circ$ , with nitrous acid (*Wohl*, Ber. 33, 2736). **Phenyl-ethyl-hydrazine**,  $\text{PhCH}_2\text{CH}_2\text{NHNH}_2$ , b.p.  $137\text{--}139^\circ$  (12–13 mm.), is obtained by the action of hydrazine on phenyl-ethyl chloride (*Votocek*, Tchec. 4, 274).

*sym*-Dibenzyl-hydrazine,  $\text{PhCH}_2\text{NHNHCH}_2\text{Ph}$ , m.p.  $65^\circ$ , is obtained by reducing benzylidene-azine (p. 273) more vigorously with sodium and alcohol. This reaction can be partially reversed by oxidising agents (*Curtius*, Ber. 28, 2345; J. pr. 58, 369).

*as*-Dibenzyl-hydrazine,  $(\text{PhCH}_2)_2\text{N}\cdot\text{NH}_2$ , m.p.  $65^\circ$ , is produced by the action of hydrazine hydrate on benzyl chloride, or by reduction of dibenzyl-nitrosamine (p. 257), with zinc dust and acetic acid. It is oxidised by mercuric oxide to a tetrazene, m.p.  $97^\circ$ , but under other reaction conditions, dibenzyl,  $\text{PhCH}_2\text{--CH}_2\text{Ph}$ , seems to be formed, nitrogen being evolved (*Busch*, Ber. 33, 2701; *Curtius*, Ber. 34, 552).

*sym*-Benzyl-phenyl-hydrazine,  $\text{PhCH}_2\text{NHNHPh}$ , m.p.  $35^\circ$ , b.p. about  $290^\circ$ , is obtained by reducing benzylidene-phenylhydrazone with sodium amalgam in alkaline solution. In air it readily reverts to the phenylhydrazone (*Schlenk*, J. pr. 78, 49). *as*-Benzyl-phenyl-hydrazine,  $\text{PhCH}_2\text{N(Ph)NH}_2$ , m.p.  $26^\circ$ , is obtained by the action of phenyl-hydrazine on benzyl chloride. It is used with advantage for isolating sugars as hydrazones (*Ruff*, Ber. 32, 3234; *Ofner*, Mo. 25, 593). On oxidation it is converted into dibenzyl-diphenyl-tetrazene,  $\text{PhCH}_2\text{--(Ph)N}\cdot\text{N:N}\cdot\text{N(Ph)CH}_2\text{Ph}$ , m.p.  $145^\circ$ , and this, when heated in xylene, is decomposed into nitrogen and *sym*-dibenzyl-diphenyl-hydrazine,  $\text{PhCH}_2\text{(Ph)N}\cdot\text{N(Ph)CH}_2\text{Ph}$ , b.p.  $181^\circ$  (11 mm.) (*Franzen*, Ber. 39, 2566).

**BENZYL-DIAZO COMPOUNDS, BENZYL TRIAZINES, AND BENZYL AZIDES**. **Benzyl-potassium diazotate**,  $\text{PhCH}_2\text{N:NOK(?)}$ , is obtained by the

action of very concentrated aqueous caustic potash on nitroso-benzyl urethane,  $\text{PhCH}_2\text{N}(\text{NO})\text{COOC}_2\text{H}_5$ . It is a white crystalline powder, decomposing into caustic potash and phenyl-diazomethane,  $\text{PhCHN}_2$ , on simply moistening with water. The latter, a reddish-brown oil, breaks down on distillation into nitrogen and stilbene,  $\text{PhCH}:\text{CHPh}$ , on heating with water, into nitrogen and benzyl alcohol, with alcohol into nitrogen and benzyl ether, and with hydrochloric acid into nitrogen and benzyl chloride (*Hantzsch*, Ber. 35, 903; cf. diazomethane, Vol. I, p. 251).

**Sodium benzyl-isodiazotate**,  $\text{PhCH}_2\text{N}:\text{NONa}$ , forms colourless needles. It is produced by the action of ethyl nitrite and sodium methoxide on *as*-nitroso-benzylhydrazine, nitrous oxide being given off. It is completely different from normal sodium benzylidiazotate. It dissolves unchanged in cold water, but on heating, or with dilute acids, it decomposes into nitrogen and benzyl alcohol. When reduced it gives benzyl-hydrazine, and on oxidation benzyl-nitramine,  $\text{PhCH}_2\text{NHNO}_2$ , m.p. 39°, is formed. The action of aluminium and sodium hydroxide on the latter re-forms the isodiazotate (*Thiele*, Ann. 376, 255).

**Benzyl-methyl-triazene**,  $\text{PhCH}_2\text{N}:\text{N}\cdot\text{NHCH}_3$ , is a colourless oil, as unstable as the aliphatic diazo-compounds (Vol. I, p. 204), and decomposed even by carbon dioxide. It is obtained by the action of magnesium methyl iodide on benzyl azide (see below). Cuprous salt, m.p. 114°, pale-yellow grains; silver salt, m.p. 125°, colourless needles (*Hantzsch*, Ber. 28, 684).

**Benzyl-phenyl-triazene**,  $\text{PhCH}_2\text{NH}:\text{N}:\text{NPh}$ , or  $\text{PhCH}_2\text{N}:\text{N}\cdot\text{NHPh}$ , m.p. 75°, colourless leaflets, is obtained by acting on benzyl azide with ethyl magnesium bromide, or phenyl azide (p. 132) with benzyl magnesium chloride. It decomposes when acted upon by dilute hydrochloric acid into benzyl chloride, aniline hydrochloride, and nitrogen (*Dimroth*, Ber. 38, 682).

**Benzyl azide**,  $\text{PhCH}_2\text{N}_3$ , b.p. 74° (11 mm.), is obtained from benzyl-nitroso-hydrazine,  $\text{PhCH}_2\text{N}(\text{NH}_2)(\text{NO})$ , (see above), by boiling with dilute sulphuric acid, by the action of sodium azide on benzyl chloride, and by the action of silver azide on benzyl iodide. It is a very stable ester of hydrazoic acid, although moderately concentrated sulphuric acid decomposes it with liberation of nitrogen and the formation of (1) benzaldehyde and ammonia; (2) aniline and formaldehyde; (3) benzylamine and nitrous oxide (?), and (4) benzyl alcohol and hydrazoic acid (*Curtius*, J. pr. 63, 428; Ber. 35, 2229; Ber. 55, 1565).

**BENZYL-HYDROXYLAMINES.**  $\alpha$ -Benzyl-hydroxylamine,  $\text{PhCH}_2\cdot\text{ONH}_2$ , b.p. 123° (50 mm.), is best obtained by hydrolysing benzyl-acetoxime,  $\text{PhC}\cdot\text{H}_2\text{ON}:\text{C}(\text{CH}_3)_2$ , with hydrochloric acid.  $\alpha$ -*p*-Chloro-benzyl-hydroxylamine, m.p. 38°, b.p. 128° (17 mm.), and  $\alpha$ -*p*-bromo-benzyl-hydroxylamine, m.p. 37°, b.p. 133° (10 mm.), are prepared in a similar way.  $\alpha$ -Benzyl-hydroxylamine, when heated in a sealed tube, partly breaks down into ammonia, water, and benzaldoxime-benzyl-ether (p. 274). With thionyl chloride,  $\text{SOCl}_2$ , it gives *thionyl-benzyl-hydroxylamine*,  $\text{PhCH}_2\text{ON}:\text{SO}$ , b.p. 154° (50 mm.), and with carbonyl chloride it gives *dibenzyl-oxyurea*,  $(\text{PhCH}_2\text{ONH})_2\text{CO}$ , m.p. 88°. With formimino-ether hydrochloride, *dibenzyl-formhydroxamoylamine*,  $\text{PhCH}_2\text{ONH}\cdot\text{CH}:\text{NOCH}_2\text{Ph}$ , m.p. 42°, is formed (*Michaelis*, Ber. 26, 2155; *Schroeter*, Ber. 33, 1975). With benzyl chloride, it gives  $\alpha$ , $\beta$ -dibenzyl-hydroxylamine,  $\text{PhCH}_2\text{O}\cdot\text{NHCH}_2\text{Ph}$ , a liquid, and *tribenzyl-hydroxylamine*,  $\text{PhCH}_2\text{ON}(\text{CH}_2\text{Ph})_2$ , also a liquid.

$\beta$ -Benzyl-hydroxylamine,  $\text{PhCH}_2\cdot\text{NHOH}$ , m.p. 57°, is formed when  $\beta$ , $\beta$ -dibenzyl-hydroxylamine is acted upon with hydrochloric acid. With benzyl chloride it gives  $\beta$ , $\beta$ -dibenzyl-hydroxylamine,  $(\text{PhCH}_2)_2\text{NOH}$ , m.p. 123° (*Lindner*, Ann. 275, 133). It combines with aldehydes to form *N*-benzyl-aldoximes (p. 274). With oxidising agents, such as bromine water or chromic acid, it gives chiefly *bis-nitrosobenzyl*,  $(\text{PhCH}_2\text{NO})_2$ , in addition to benzaldoxime, and other products. *bis*-Nitrosobenzyl is converted into benzylidene-benzoyl-hydrazine and its decomposition products by hydrochloric acid:  $(\text{PhCH}_2\text{NO})_2 \rightarrow \text{PhCH}:\text{N}\cdot\text{NHCOPh} + \text{H}_2\text{O}$ . In air,  $\beta$ -benzyl-hydroxylamine oxidises chiefly to benzaldoxime (*Bamberger*, Ber. 33, 3193; *Behrens*, Ann. 323, 265). When  $\beta$ -benzyl-hydroxylamine is heated with formic acid,  $\beta$ -benzyl-formohydroxamic acid,  $\text{PhCH}_2\text{N}(\text{OH})\cdot\text{CHO}$ , m.p. 49–50°, is produced.  $\beta$ -Dibenzyl-hydroxylamine gives *N*-benzyl-benzaldoxime (p. 274) on oxidation. Di-substituted benzyl-hydroxylamines,  $\text{Ar}\cdot\text{CH}_2\text{N}(\text{OH})\text{Alk}$ , or  $(\text{Ar})_2\text{CHN}(\text{OH})\text{Alk}$ , are formed when *N*-alkyl-ethers of oximes ("nitrones"),  $\text{Ar}\cdot\text{CH}:\text{N}(\text{O})\text{Alk}$  and  $(\text{Ar})_2\text{C}:\text{N}(\text{O})\cdot\text{Alk}$ , respectively, are reduced catalytically. **Benzyl-phenyl-hydroxylamine**,

$\text{PhCH}_2\text{N}(\text{OH})\text{Ph}$ , m.p. about  $85^\circ$ , is obtained from phenyl-*N*-phenyl nitron (Cusmano, Gazz., 51, II, 306).

**SUBSTITUTED BENZYL ALCOHOLS** have been obtained from substituted benzyl chlorides by boiling with aqueous potash or potassium carbonate (Söderbaum, Ber. 25, 3290), or from their acetates, or by the electrolytic reduction of substituted benzoic acids. Some of them have been obtained from the corresponding aldehydes by the action of alcoholic potash, e.g., *m*-nitrobenzyl alcohol.

| Compound             | ortho-                    | meta-                     | para-             |
|----------------------|---------------------------|---------------------------|-------------------|
| Chlorobenzyl alcohol | m.p. $74^\circ$           | b.p. $234^\circ$          | m.p. $75^\circ$   |
| Chlorobenzyl bromide | b.p. $120^\circ$ (10 mm.) | .....                     | m.p. $48.5^\circ$ |
| Bromobenzyl alcohol  | m.p. $80^\circ$           | b.p. $252-253^\circ$      | m.p. $77^\circ$   |
| Bromobenzyl bromide  | m.p. $30^\circ$           | m.p. $41^\circ$           | m.p. $61^\circ$   |
| Iodobenzyl alcohol   | .....                     | b.p. $154^\circ$ (10 mm.) | m.p. $72^\circ$   |
| Nitrobenzyl alcohol  | m.p. $74^\circ$           | m.p. $27^\circ$           | m.p. $93^\circ$   |
| Nitrobenzyl chloride | m.p. $48^\circ$           | m.p. $46^\circ$           | m.p. $72^\circ$   |
| Nitrobenzyl bromide  | m.p. $46^\circ$           | m.p. $58^\circ$           | m.p. $99^\circ$   |

*o*-Nitrobenzyl alcohol has also been obtained by electrolytic oxidation of *o*-nitrotoluene (Lemoult, C.r., 132, 885); and *p*-nitrobenzyl alcohol has been obtained by oxidation of *p*-nitrotoluene with manganese dioxide and sulphuric acid (Ger. Pat. 212,949). Zinc dust and aqueous ammonium chloride reduce *o*-nitrobenzyl alcohol to *o*-hydroxyl-aminobenzyl alcohol,  $\text{HONH}[2]\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ , m.p.  $104^\circ$ . When the latter is oxidised with chromic acid, it gives *o*-azoxybenzyl alcohol,  $\text{ON}_2(\text{C}_6\text{H}_4\text{CH}_2\text{OH})_2$ , m.p.  $123^\circ$ , but with permonosulphuric acid or ferric chloride it gives *o*-nitrosobenzyl alcohol,  $\text{ON}[2]\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ , m.p.  $101^\circ$ . When this is boiled with water, it loses water, and gives anthranil (Bamberger, Ber. 36, 836). It is the intermediate link in the production of anthranilic acid by heating *o*-nitrotoluene with aqueous alkali (p. 63).

*p*-Nitrophenyl-ethyl alcohol, m.p.  $64^\circ$ , is obtained by the action of nitrous acid on *p*-nitrophenyl-ethylamine hydrochloride (Ehrlich, Ber. 45, 2428). 1,2,4,5-Trinitrophenyl-ethyl alcohol, m.p.  $112^\circ$ , is obtained by the action of 40% formaldehyde on 1,2,4,5-trinitro-toluene, in the presence of sodium hydroxide and potassium carbonate (Vender, Gazz. 45, II, 97). *m*-Azoxybenzyl alcohol, m.p.  $86^\circ$ , is obtained by heating *m*-nitrobenzaldehyde with sodium arsenite (Kranz, Am. Pharm. 19, 461). *p*-Azoxybenzyl alcohol, m.p.  $222-223^\circ$ , is obtained by reduction of *p*-nitrobenzyl alcohol with zinc and ammonium chloride in alcoholic solution. The *o*-isomer is obtained similarly (Cumming, J. Glasgow, 1932). *m*-Azobenzyl alcohol,  $\text{N}_2(\text{C}_6\text{H}_4\text{CH}_2\text{OH})_2$ , orange-yellow needles, m.p.  $117^\circ$ , is obtained by the action of zinc dust and sodium hydroxide on *m*-nitrobenzaldehyde. *o*-Hydrazobenzyl alcohol,  $\text{H}_2\text{N}_2(\text{C}_6\text{H}_4\text{CH}_2\text{OH})_2$ , a white powder, m.p.  $104^\circ$ , is obtained by a similar method from *o*-nitrobenzaldehyde (Sen, Indian. J. 9, 403).

Aminobenzyl alcohols are formed by the reduction of nitrobenzyl alcohols, and by the electrolytic reduction of nitro- and amino-benzoic acids in acid solution.

*p*-Aminobenzyl alcohol, m.p.  $64^\circ$ , passes into its anhydro-form,  $\left(\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{NH} \end{array}\right)_2$ ,

when treated with acids. This compound, and a number of its derivatives, have also been obtained by the direct action of formaldehyde on the corresponding anilines in the presence of acids (Goldschmidt, Chem. Z. 24, 284; Löb, Ber. 31, 2037; Meyer, Ber. 33, 250; 35, 739). *p*-Aminophenyl-ethyl alcohol, m.p.  $171^\circ$ , is obtained by the action of tin and hydrochloric acid on the *p*-nitro-compound (Ehrlich, Ber. 45, 2438).

*p*-Amino-benzylamine,  $\text{NH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$ , b.p.  $269^\circ$ ; *p*-acetyl-amino-*N*-chloroacetyl-benzylamine,  $\text{CH}_3\text{CONHC}_6\text{H}_4\text{CH}_2\text{NHCOCH}_2\text{Cl}$ , has been obtained by nuclear synthesis, viz., the condensation of acetanilide with methylol-chloroacetamide,  $\text{CH}_2\text{ClCONH}\cdot\text{CH}_2\text{OH}$ , under the action of concentrated sulphuric acid. Boiling hydrochloric acid removes the acetyl and chloroacetyl groups (Einhorn, Ann. 343, 299).

*p*-Amino-benzylaniline,  $\text{NH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NHPh}$ , a viscous oil, obtained by the action of anhydro-formaldehyde-aniline on aniline (p. 84), readily changes to diamino-diphenyl-methane (Ger. Pats. 84,934 and 108,064). *p*-Nitrobenzylamine see Paal, Ber. 30, 61.

*m*-Aminobenzyl alcohol,  $\text{NH}_2[3]\text{C}_6\text{H}_4[1]\text{CH}_2\text{OH}$ , m.p.  $92^\circ$ , is obtained by electrolytic reduction of *m*-nitrobenzoic acid (Mettler, Ber. 38, 1751). *o*-Aminobenzyl-alcohol,  $\text{NH}_2[2]\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ , m.p.  $82^\circ$ , b.p.  $160^\circ$  (10 mm.), is formed by the reduction of *o*-nitrobenzyl alcohol (p. 261), or from anthranil (p. 278) by reduction with zinc dust and hydrochloric acid, or sodium sulphide (Reissert, Ber. 61, 2555). It is also obtained by reduction of ethyl anthranilate with sodium amalgam in acid solution (Langguth, Ber. 38, 2062), or by electrolytic reduction of *o*-nitrobenzoic, or anthranilic acid (Mettler, loc. cit.). The best yield (88%) is obtained by reducing *o*-nitrobenzyl alcohol with sodium hydrosulphite (Reissert, Ber. 61, 2555).

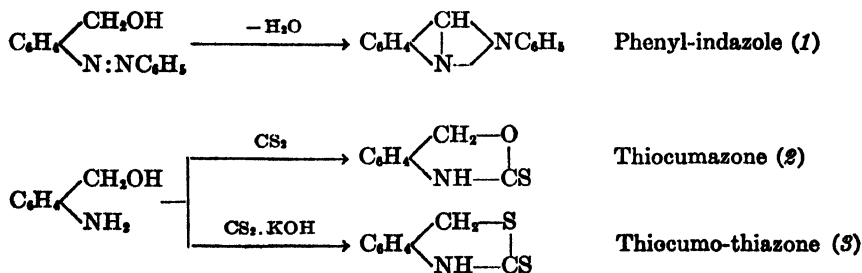
*O*-Acetyl-*o*-aminobenzyl alcohol,  $\text{NH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OCOCH}_3$ , is an oil with a smell resembling that of aniline, obtained by reducing *o*-nitrobenzyl acetate. Its hydrochloride melts at  $116^\circ$ . The free base is unstable, and changes on standing, and more rapidly on heating, to the crystalline *N*-acetate,  $\text{CH}_3\text{CONHC}_6\text{H}_4\text{CH}_2\text{OH}$ , m.p.  $116^\circ$ . Cold hydrobromic acid converts the latter into *μ*-methyl-benzometozazine hydrobromide (see below). This takes up water on standing in aqueous solution, and decomposes to give *O*-acetyl-*o*-aminobenzyl alcohol (Auwers, Ber. 37, 2249).

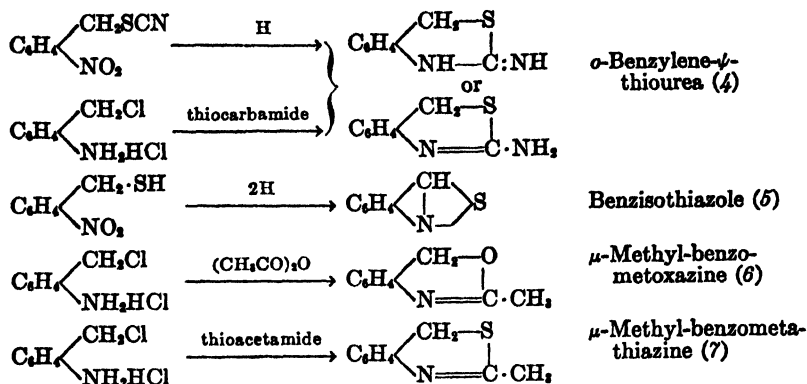
*Formation of heterocyclic compounds from derivatives of o-aminobenzyl alcohol* (see Vol. IV).—Like the *o*-diamines (p. 106), *o*-aminophenols (p. 205), and *o*-aminothiophenols (p. 214), many derivatives of *o*-aminobenzyl alcohol, and some of *o*-nitrobenzyl alcohol (which give *o*-aminobenzyl alcohol on reduction) are able to form heterocyclic compounds. Heterocyclic compounds have been obtained, for example, from the following derivatives of these two alcohols:

*o*-Aminobenzyl alcohol combines with nitroso-benzene to form benzene-azo-*o*-benzyl alcohol,  $\text{PhN}:\text{NC}_6\text{H}_4\text{CH}_2\text{OH}$ , m.p.  $78^\circ$ , and this, when heated with sulphuric acid, gives phenyl-indazole (1 below) (Bamberger, Ber. 44, 1967). When boiled with carbon disulphide in alcoholic solution, *o*-aminobenzyl alcohol gives thiocumazone, or, in presence of alkali, thiocumo-thiazone (3 below). Similar rings have been obtained from urea derivatives of *o*-aminobenzyl alcohol (Paal, Ber. 27, 1866, 2413, 2437).

*o*-Nitrobenzyl thiocyanate,  $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{S}\cdot\text{CN}$ , m.p.  $75^\circ$  (Cassirer, Ber. 25, 3028), gives *o*-benzylene- $\psi$ -thiourea (4) on reduction; sulphuric acid converts it into *o*-nitrobenzyl-carbamine-thiolic ester,  $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{S}\cdot\text{CONH}_2$ , m.p.  $116^\circ$ . This is hydrolysed by hydrochloric acid to *o*-nitrobenzyl-mercaptopan,  $\text{NO}_2[2]\text{C}_6\text{H}_4[1]\text{CH}_2\text{SH}$ , m.p.  $43^\circ$ ; both these compounds give benzisothiazole (5) on reduction (Gabriel, Ber. 28, 1027; 29, 160; 31, 2185).

*o*-Aminobenzyl chloride hydrochloride,  $\text{HCl}\cdot\text{NH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ , is formed by the action of concentrated hydrochloric acid on *o*-aminobenzyl alcohol. This salt is converted into poly-*o*-benzylene imide,  $(\text{C}_7\text{H}_7\text{N})_x$ , by the action of caustic potash (Lellmann, Ber. 19, 1611; Thiele, Ber. 28, 918); into *μ*-methyl-benzometozazine (6) by acetic anhydride; into *μ*-methyl-benzometathiazine (7) by thioacetamide; and into *o*-benzylene- $\psi$ -thiourea (4) by thiourea (Gabriel, Ber. 27, 3515; 28, 1039):





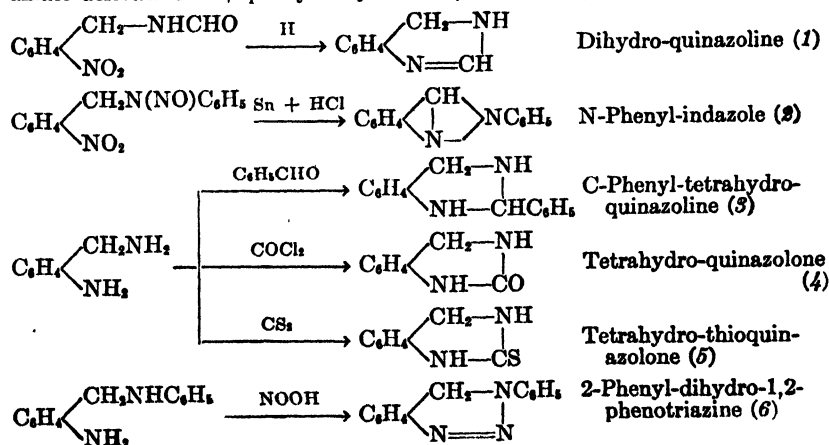
The anhydride of an *o*-benzyl alcohol sulphonic acid, or *sulphobenzide*,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{SO}_2 \\ \text{CH}_2 \end{array} \text{O}$ , m.p. 113°, is obtained by the reduction of *o*-sulphobenzoyl chloride (p. 332), just as phthalide (p. 376) is obtained from phthalyl chloride. It is also formed by reduction of the product of interaction of *o*-benzaldehyde sulphonic acid (p. 280) with phosphorus pentachloride (*List*, Ber. 31, 1666).

*o*-Nitrobenzylamine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{NH}_2$ , obtained from *o*-nitrobenzyl phthalimide, is a liquid. *o*-Nitrobenzyl formamide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{NHCHO}$ , m.p. 89°, gives *dihydro-quinazoline* (1 below) on reduction. For the reduction of other acyl compounds of *o*-nitrobenzylamine, see *Gabriel*, Ber. 36, 806; 45, 713.

*o*-Nitrobenzylaniline,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{NHPh}$ , m.p. 44° (*Lellmann*, Ber. 19, 1607). Alkali sulphides reduce *o*- and *p*-nitrobenzylanilines to amino-benzylidene-anilines (Ger. Pat. 99,542). *o*-Nitrobenzyl-phenyl-nitrosamine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{N(NO)Ph}$ , is reduced by tin and hydrochloric acid to *N*-phenyl-indazole (2) (*Busch*, Ber. 27, 2899). *o*-Amino-benzylamine, *o*-benzylene diamine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{NH}_2$ , crystallises in lancets. It is obtained from *o*-nitrobenzylamine. It condenses with aldehydes. Thus, with benzaldehyde it gives *phenyl-tetrahydro-quinazoline* (3). With phosgene it gives *tetrahydro-quinazolone* (4), and with carbon disulphide, *tetrahydro-thioquinazolone* (5) (*Busch*, J. pr. 51, 113). *o*-Amino-benzylaniline,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{NHPh}$ , m.p. 86°, gives 2-phenyl-dihydro-1,2-phenotriazine (6), with nitrous acid (*Busch*, Ber. 25, 448).

For homologues of *o*-aminobenzylaniline see Ger. Pat. 105,797. Nitro- and amino-derivatives of  $\beta$ -phenyl-ethyl alcohol, see *Sablaty*, Ber. 49, 3.





## 2. Aromatic Mono-aldehydes

The aromatic mono-aldehydes are the primary oxidation products of the aromatic monohydric alcohols. They resemble the aliphatic aldehydes in all reactions due to the CHO group.

*Methods of formation.*—1. By the oxidation of primary monohydric alcohols. 1a. By a double decomposition which takes place when an alcohol is heated with an aldehyde in the presence of a metallic alkylate (see p. 250). Thus: cinnamic aldehyde and benzyl alcohol give benzaldehyde and cinnamyl alcohol (*Ponndorf*, *Angew.* 39, 138). 1b. By catalytic oxidation of acids by means of finely divided silver (*Moureu*, *C.r.* 170, 258). 1c. Oxidation of chlorides of the type  $\text{Ar}\cdot\text{CH}_2\text{Cl}$  with alkali dichromate and alkali hydroxide or carbonate:  $3\text{ArCH}_2\text{Cl} + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{NaOH} = 3\text{ArCHO} + 3\text{NaCl} + \text{Cr}_2\text{O}_3 + 2\text{H}_2\text{O}$  (*Ger. Pat.* 347,583). 1d. The action of aralkylamines on nitro-halogen-benzenes, which contain a reactive halogen atom, converting the aryl-methyl-amino-compounds obtained into azomethines, and hydrolysing the latter by means of mineral acids, thus giving aldehydes (*Ger. Pat.* 482,837).

2. Aromatic acids are reduced to aldehydes by: 2a. distilling their calcium or barium salts with calcium or barium formate; 2b. heating their vapours in an atmosphere of carbon dioxide with a hydrogenation catalyst (*Br. Pat.* 267,925); 2c. reducing their chlorides in boiling benzene in the presence of certain catalysts, such as  $\text{Pd}/\text{BaSO}_4$ , Ni, etc. (*Rosenmund*, *Ber.* 51, 585; 56, 1481; *Sw. Pat.* 92,404), or by treating the chlorides with diazomethane, and acetic acid, reducing the product, and finally treating with lead tetracetate (*Grundmann*, *Ann.* 524, 31); 2d. converting acid anilides into anil chlorides of the type  $\text{Ar}\cdot\text{CCl}:\text{NPh}$  (p. 307), replacing the chlorine atom by hydrogen by treatment with stannous chloride in ether solution, and hydrolysing the aniline double salt which is produced (*Sonn*, *Ber.* 52, 1927); 2e. reducing acid nitriles with stannous chloride and hydrochloric acid in ether; a double salt of the aldehyde imine is formed, and is hydrolysed, as in the last method, to the aldehyde:  $\text{ArCN} \rightarrow \text{Ar}\cdot\text{CCl}:\text{NH} \rightarrow \text{Ar}\cdot\text{CH}:\text{NH} \rightarrow \text{Ar}\cdot\text{CHO}$  (*Stephen*, *J.* 127, 1874); 2f. heating aromatic dicarboxylic anhydrides with reducing gases in the presence of a catalyst (*Ger. Pat.* 526,482).

3. Chloro-aldehydes, such as  $\text{PhCHCl}_2$ , are treated with water, preferably in the presence of sodium carbonate, lime, or lead oxide, or they are heated with anhydrous oxalic acid. 4. Benzaldehyde is produced industrially by oxidising benzyl chloride with lead nitrate in an atmosphere of carbon dioxide. 5. Hydrocarbons can be converted into aldehydes by means of chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ . Addition compounds of the type  $\text{PhCH}_3(\text{CrO}_2\text{Cl}_2)_2$  are first formed. They are brown powders, which when acted upon by a trace of water decompose forming aldehydes (*Étard's reaction*, *Stuart*, *J.* 53, 803; *Sword*, *Chem. News*, 133, 1; *Bornemann*, *Ber.* 17, 1462; *Weiler*, *Ber.* 32, 1050).

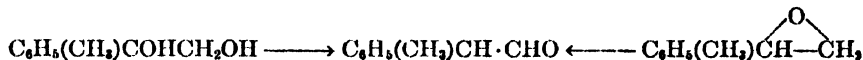
When toluene and its substitution products are oxidised with chromic acid in the presence of acetic anhydride at  $0^\circ$ , *ortho*-aldehyde diacetates, such as  $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{CH}(\text{OCOCH}_3)_2$ , and  $\text{C}_6\text{H}_4[\text{CH}(\text{OCOCH}_3)_2]_2$ , are obtained (*Reich*, *Bull.* 19, 287). Other reagents which will oxidise alkyl-benzenes to aromatic aldehydes in the cold are manganese dioxide and sulphuric acid, manganic sulphate, ceric oxide and sulphuric acid (*Ger. Pats.* 121,788, 174,238, and 175,295; *Fourmier*, *C.r.* 133, 694). Copper sulphate and nickel sulphate are sometimes added in the oxidation of toluene with manganese dioxide and sulphuric acid to accelerate the reaction (*Jevdokimov*, *C.* 1930, 1, 820; *Russ. Pat.* 10,440). Alkyl-benzenes have

been oxidised electrolytically to aldehydes (*Law*, Chem. News, 72, 66; *Mann*, Am. Electrochem. Soc., 1925, 47), or catalytically with oxidising gases in the presence of molybdenum, uranium, or copper oxides (Sw. Pat. 8,884; Br. Pats. 189,091 and 189,107), or by means of sodium hypochlorite in an autoclave at 150°, in the presence of iron compounds (Czech. Pat. 31,736).

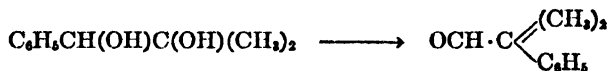
6. Olefine-benzenes are treated with ozone, which adds on at the double bond. Hydrolysis of the ozonide formed gives an aldehyde (*Harries*, Ber. 37, 842; Ann 343, 311; *Klages*, Ber. 37, 2304; *Semmler*, Ber. 41, 2751):



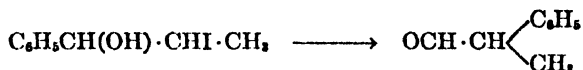
7. Primary-secondary and primary-tertiary aromatic ethylene glycols, when heated with dilute sulphuric acid, and the corresponding ethylene oxide when heated alone, give aldehydes (*Fourneau*, C.r. 141, 662; *Strömer*, Ber. 39, 2288):



The secondary-tertiary phenyl-ethylene glycols give aldehydes with migration of the phenyl group:



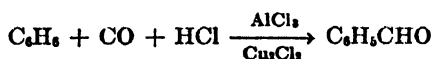
Iodohydrins of some olefine-benzenes give aldehydes when treated with silver nitrate or mercuric oxide (*Tiffeneau*, Ann. chim. phys. [8], 10, 322; 16, 237):



Here again, there is a migration of the phenyl group.

8. Aldehydes are formed when phenyl-nitromethanes (p. 256) are reduced, and when  $\beta$ -benzyl-hydroxylamines are oxidized. Oximes of the aromatic aldehydes are first formed, and the aldehydes themselves are produced by hydrolysis of the oximes (*Pinnow*, Ber. 32, 898).

9a. The aldehydes are obtained synthetically by the action of carbon monoxide and hydrogen chloride, preferably under pressure, on aromatic hydrocarbons. The presence of sulphuric acid, cuprous chloride, nickel chloride, other anhydrous metallic chlorides, and aluminium chloride or bromide is necessary:



(*Gattermann*, Ann. 347, 347; *Korczynski*, Bull. 29, 459; Br. Pat. 334,009; *Coleman*, *Craig*, Org. Synth. 12, 80).

Instead of carbon monoxide and cuprous chloride, iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , which readily liberates carbon monoxide, may be used. The reaction is best carried out in nitrobenzene (Ger. Pat. 403,489). There are many modifications of this Gattermann synthesis, among which may be mentioned the action of formyl-substituted secondary amines, or formamide and aluminium chloride on benzene hydrocarbons (Ger. Pats. 514,415, 519,444, and 519,806).

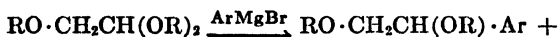
9b. When benzene and mercury fulminate,  $(\text{C}:\text{NO})_2\text{Hg}$ , are treated with hydrated aluminium chloride, benzaldoxime,  $\text{PhCH}:\text{NOH}$ , is formed. If anhydrous aluminium chloride is used in this reaction, nitriles are chiefly formed (*Scholl*, Ber. 36, 322). 9c. Aldehydes are also obtained by condensing hydrocarbons with formyl derivatives of secondary amines, e.g., formyl-methyl-aniline, in the presence of aluminium chloride, etc. These condensation products yield aldehydes with water (Fr. Pat. 648,069; Ger. Pats. 514,415 and 510,444).

10a. Aromatic aldehydes are formed by the action of aryl-magnesium halides on an excess of ethyl formate:

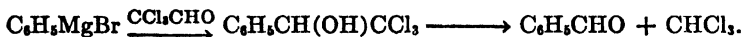


If orthoformic ester is used, acetals are obtained, which can be converted into the corresponding aldehydes by hydrolysis with boiling acids. In some cases, *ethoxy-methylene-aniline*,  $\text{PhN}:\text{CHOEt}$ , has been used with good results instead of ethyl formate. In this case benzylidene-anilines (*q.v.*) are the first products. These readily give aldehydes on boiling with dilute acids (*Gattermann*, Ber. 36, 4152; Ann. 393, 215; *Tshitshibabin*, Ber. 37, 186; *Bodrour*, C.r. 138, 92, 700; *Monnier*, J. 89, 273; Ger. Pat. 175,573).

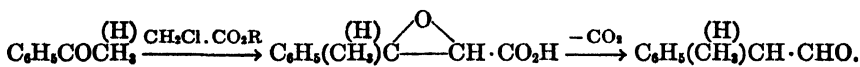
10b. When aliphatic alkoxy-acetals, of the type  $\text{RO}\cdot\text{CH}_2\text{CH}(\text{OR})_2$ , interact with aryl-magnesium halides, one alkoxy in the acetal group is replaced by an aryl group, and a mixture of arylated ethers and vinyl ethers is produced. When treated with dilute sulphuric acid, both these products pass, first into an unstable vinyl alcohol, and then into an aldehyde:



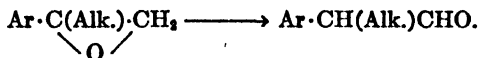
11. The condensation products obtained from aryl-magnesium halides and chloral,  $\text{Ar}\cdot\text{CHOH}\cdot\text{CCl}_3$ , decompose on boiling with aqueous potassium carbonate into chloroform and aldehydes (*Savariau*, C.r. 146, 297; *Hebert*, Bull. 27, 45):



12. *Aryl-glycidic acids* (p. 420), obtained by condensing aromatic aldehydes and ketones with chloroacetic ester and sodium ethylate or sodamide, decompose readily into aldehydes and carbon dioxide (*Darzens*, C.r. 139, 1214; *Claisen*, Ber. 38, 699):

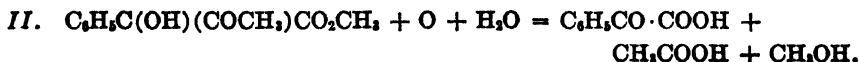
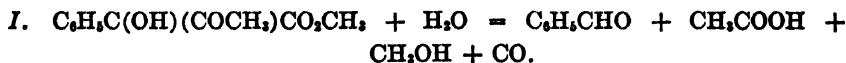


13. Aryl- and aralkyl-magnesium halides condense with  $\alpha$ -chloroketones, to give chlorhydrins. When these are treated with sodium hydroxide, they lose hydrogen chloride, and become aralkylene oxides, which, under the further action of sodium hydroxide, are converted into aldehydes (C. 1932, I, 1337).



14. Benzoyl-formic acid,  $\text{PhCOCO}_2\text{H}$ , and its homologues, which are readily obtainable by synthetic methods, give benzylidene-anilines when heated with aniline. These are readily broken down to aldehydes and aniline (*Fournier*, C.r. 136, 357, and others).

15.  $\alpha,\beta$ -Diketo-carboxylic esters, or mesoxalic ester, condense with benzene hydrocarbons, tertiary anilines or phenols. The resulting *acyl-phenyl-glycollic esters* (p. 410) and *phenyl-tartronic esters* (p. 436) can be converted into aldehydes, either by heating with concentrated sulphuric acid (equation I), or by oxidising them with cupric acetate to benzoyl-formic acids (equation II), and decomposing these as explained in the preceding paragraph (*Guyot*, C.r. 149, 788):



16. When benzyl-sulphone-acylphenyl-hydrazones are decomposed with caustic potash, they yield aryl-aldehydes (*McFadyen*, J. 1936, 584):



*Properties.*—Benzaldehyde and most of its homologues are liquids with an aromatic odour. They give a silver mirror with ammoniacal silver nitrate. (1) They are readily oxidised to carboxylic acids. (2) With caustic alkalis they give alcohols and carboxylic acids. When benzaldehyde, for example, is treated with sodium ethylate, or better with sodium benzyolate, disproportionation occurs, with formation of benzyl benzoate, a reaction known as Cannizzaro's reaction. This reaction seems to be peculiar to aldehydes in which the CHO group is attached directly to the ring. (3) Nascent hydrogen reduces the aldehydes to alcohols, two aldehyde residues combining to give a *hydrobenzoin* (p. 563). The acetals of those aldehydes of which the CHO group is directly attached to the benzene ring can be reduced catalytically to benzene hydrocarbons (*Kariyou*, J. Pharm. Japan, 1923). (4) They form addition products with alkali sulphites and sulphurous acid.

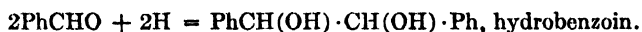
(5) With hydroxylamine they form *aldoximes*, which form interesting isomerides. (6) With hydrogen cyanide, *cyanhydrins* are produced. (7) With phenylhydrazine, *phenylhydrazones* are formed. (8) With primary amines, *aldehyde-imines*, or *Schiff's bases*, are produced. (9) With nitro-hydroxylamates, e.g., NaON:NOONa, and benzene-sulphydroxamates, *hydroxamic acids* are formed (*Angeli*, Gazz. 34, I, 56). (10) By the action of phosphorus pentachloride, the aldehyde oxygen atom is replaced by two chlorine atoms. (11) Chlorine itself substituted the aldehyde hydrogen atom. (12) Hot hydrogen sulphide gives *kyanidines* (Vol. IV). (13) When aldehydes of the type  $\text{Ar} \cdot \text{CH}(\text{Alk}) \cdot \text{CHO}$  are heated they are converted into ketones of the formula  $\text{Ar} \cdot \text{CH}_2\text{CO} \cdot \text{Alk}$  (C. 1922, I, 2026). (14) When heated with orthoformic ester, or orthosilicic ester, and a small amount of acid, they give acetals (Ger. Pat. 404,256). (15) They add on nitromethane, with formation of  $\omega$ -nitro-styrenes (C. 1932, I, 1379). (16) They combine at ordinary temperatures with acyl chlorides, giving unstable double compounds, some of which are solids (*Adams*, Am. 40, 1732). (17) For the action of Grignard reagents on aldehydes, see *Marshall*, J. 105, 527. (18) The aldehydes condense with hippuric acid to give cyclic compounds, called *azlactones* or *oxazolones*. These are decomposed by hydrogen iodide into  $\alpha$ -amino-acids containing two carbon atoms more than the original aldehydes.

They are readily oxidised, and some polymerise readily. For their identification by means of *m*-nitro- or *o*-chloro-benzhydrazide, see *Sah*, Rep. Hua 2, 347.

*Nuclear syntheses.*—(1) When aromatic aldehydes are reduced, electrolytically, or otherwise, *hydrobenzoin*s (Vol. I, p. 363) are formed, together with alcohols (*Kaufmann*, Z. Elek. 2, 365; *Law*, J. 89, 1512). The process resembles pinacone formation (Vol. I, p. 363):



(2) Under the influence of alcoholic potassium cyanide a very remarkable dimerisation occurs, resulting in the formation of *benzoins* (p. 564):

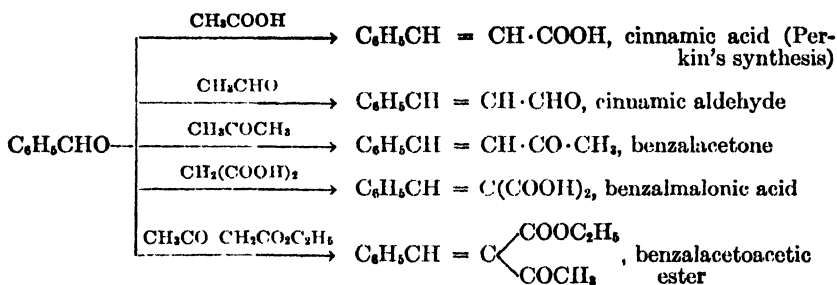


The same reaction takes place in toluene solution in the presence of a small quantity of activated magnesium (*Schorigin*, Ber. 66, 1431). For the condensation of benzyldene-aniline and benzaldehyde under the influence of potassium cyanide, see *Miller*, Ber. 29, 1729; 31, 2699.

(3) Aromatic aldehydes combine with many substances, *e.g.*, aldehydes, ketones, mono- and di-carboxylic acids, *etc.*, with the elimination of water.

These so-called condensations resemble the aldol-condensation, but in most cases water is lost, as in the formation of mesityl oxide from acetone. The usual condensing agents are: hydrogen chloride, zinc chloride, sulphuric acid, acetic acid, acetic anhydride, dilute sodium hydroxide, sodium ethoxide, baryta water, aqueous potassium acetate, primary, secondary, and tertiary bases.

Benzaldehyde readily enters into the following reactions:



With ketones, such as diethyl ketone, 2 mols. of benzaldehyde condense with formation of *pyrones*, *e.g.*,  $\text{CO} \begin{matrix} \text{CH}(\text{CH}_2) \cdot \text{CH}(\text{C}_6\text{H}_5) \\ \text{CH}(\text{CH}_3) \cdot \text{CH}(\text{C}_6\text{H}_5) \end{matrix} \text{O}$ , but with cyclic ketones, in which the grouping  $-\text{CH}_2\text{COCH}_2-$  forms part of the ring, *dibenzylidene* derivatives are usually obtained (*Wallach*, C. 1908, I, 637). For further condensation reactions, see *Dillhey*, J. pr. 130, 147.

*Pyridine* derivatives are formed when benzaldehyde and acetoacetic ester condense with ammonia or aniline; benzyldene-di-acetoacetic esters are formed when aliphatic amines are used (*Lachowicz*, Mo. 17, 343). *Triphenylmethane* derivatives are obtained with phenols and anilines.

For the removal of the CHO group as formic acid,  $\text{HCOOH}$ , by the action of alkalis, see *Lock*, Ber. 69, 2253.

**Benzaldehyde**, *bitter-almond oil*,  $\text{C}_6\text{H}_5\text{CHO}$ , m.p.  $-55^\circ$  to  $-56^\circ$ , b.p.  $179^\circ$ ,  $d_{15}$  1.050, is a colourless liquid of high refractive index, with a characteristic, pleasant smell of bitter-almond oil, which is, in fact, nearly pure benzaldehyde. It dissolves in 200 parts of water, and is miscible with alcohol and ether. In bitter-almond oil, the benzaldehyde is present as a glucoside, *amygdalin* (Vol. II, p. 365). This was first demonstrated by *Liebig* and *Wöhler* in 1831. *Amygdalin* ( $\text{C}_{20}\text{H}_{22}\text{NO}_{11}$ ) readily decomposes into benzaldehyde, *d*-glucose, and hydrocyanic acid, either on boiling with dilute mineral acids, or

on standing with the ferment *emulsin*, which is also present in bitter almonds:



Benzaldehyde was formerly prepared from amygdalin, and the *aqua amygdalarum amararum* of pharmacy, in which hydrocyanic acid is the active ingredient, is still made in this way. The reactions by which benzaldehyde is formed have been given under the general methods, above; it is obtained (1) from benzyl alcohol, (2) from calcium benzoate and calcium formate; (3) from benzylidene chloride; (4) from benzyl chloride, from which it is manufactured commercially by oxidation with lead nitrate; (5) from toluene by the action of chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ ; (6) from benzene and carbon monoxide in the presence of hydrogen chloride, cuprous chloride and aluminium chloride, or aluminium chloride alone (under pressure); (7) by the action of phenyl magnesium bromide on ethyl formate, or its derivatives.

In the description of the reactions of the aromatic aldehydes above, benzaldehyde has usually been taken as an example. It takes up oxygen from the air, forming benzoic acid. One molecule of oxygen is first taken up, and *benzoyl-hydroperoxide*,  $\text{PhCO}_2\text{H}$ , m.p.  $42-43^\circ$ , is formed (see p. 298). This reacts with a second molecule of benzaldehyde forming benzoic acid. The kinetics of this reaction, both in the light and in the dark, have been studied by *Raymond*, C.r. 191, 616; J. chim. phys. 28, 316, 421, and by *Bäckström*, J. Phys. Ch. 35, 2530. When a mixture of benzaldehyde and acetic anhydride is exposed to the air, *benzoyl acetyl peroxide* (p. 299) is formed. Sodium amalgam reduces benzaldehyde to benzyl alcohol and hydrobenzoin. Phosphorus pentachloride gives benzylidene chloride. Benzaldehyde forms an oxime, a phenylhydrazone, etc. When a little sodium ethylate or benzyolate is added to benzaldehyde, Cannizzaro's reaction takes place with evolution of a considerable amount of heat, and benzyl benzoate is formed. Benzaldehyde combines with sulphur dioxide to give a hydroxy-sulphonic acid, soluble in water, from which the aldehyde is regenerated by heating. This reaction has been used for purifying benzaldehyde (*Tshitshibabin*, Ber. 37, 850). For the detection of chlorine in commercial benzaldehyde, see *Schimmel's* Ber. 1921, 56.

**HOMOLOGOUS BENZALDEHYDES.** *o*-, *m*-, and *p*-Tolualdehydes boil at  $195^\circ$ ,  $195^\circ$ , and  $198-200^\circ$ , respectively. *o*- and *m*-Compounds have the smell of benzaldehyde, but the *p*-compound smells like pepper. For derivatives see *Haslik*, Ber. 32, 2282; *Sommer*, Ber. 33, 1073; *Quelet*, C.r. 193, 939.

**Phenyl-acetaldehyde**,  $\alpha$ -tolualdehyde,  $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ , m.p.  $33-34^\circ$ , b.p.  $206^\circ$ , is isomeric with the three tolualdehydes. It is obtained by distilling a mixture of calcium phenylacetate and calcium formate; by the action of chromyl chloride on ethyl-benzene; by the action of water on  $\alpha$ -bromo-styrene; by the action of benzyl magnesium chloride on ethyl formate or its derivatives (method of preparation, see *Gattermann*, Ber. 36, 4152); from phenyl-lactic or phenyl-glycidic acid and dilute sulphuric acid; by the action of caustic alkalies on phenyl- $\alpha$ -chloro-lactic acid,  $\text{PhCHOH}\cdot\text{CHCl}\cdot\text{COOH}$  (*Lipp*, Ber. 16, 1286; *Erlenmeyer*, Ann. 219, 179); by heating phenyl-glycerolic acid, and by heating the  $\beta$ -lactone of this acid,  $\text{PhCH(O)CH(OH)CO}$ , with water (Ger. Pat. 107,229). Phenyl-

acetaldehyde has a sweetish odour, resembling hyacinth, and is used in perfumery. It polymerises readily in contact with dilute sulphuric acid, or with 10% caustic potash, or even on standing, forming a trimer, or occasionally a dimer or hexamer (*Stobbe*, J. pr. 90, 277; *Pound*, J. Phys. Ch. 35, 1174). Odiferous cyclic acetals obtained from phenyl-acetaldehyde are described in Fr. Pat. 682,717. Heated with alcoholic potash, phenyl-acetaldehyde gives a mixture of *triphenylbenzene* and 1,3-diphenyl-cyclobutane (?) (*Stoermer*, Ber. 38, 1966). For phenyl-acetaldehydes alkylated in the nucleus, see *Späth*, Mo. 36, 1.  **$\alpha$ -Phenyl-propyl-aldehyde**, hydratropic aldehyde,  $\text{Ph}(\text{Me})\text{CH}\cdot\text{CHO}$ , b.p.  $204^\circ$ , is obtained by the action of hot, dilute sulphuric acid on *as*-phenyl-methyl-glycol (*Stoermer*, Ber. 39, 2297), or from phenyl-methyl-glycidic acid, or *as*-phenyl-methyl-ethylene oxide by heating alone or with 5% sulphuric acid (*Claisen*, Ber. 38, 704; *Noelling*, Ber. 38, 2506; *McKenzie*, Ber. 65, 804).  **$\alpha$ -Phenyl-butyraldehyde**  $\text{Ph}(\text{Et})\text{CH}\cdot\text{CHO}$ , b.p.  $211^\circ$ , is prepared from *as*-phenyl-ethyl glycol (*Stoermer*, Ber. 39, 2300).  **$\alpha$ -Propyl-phenyl-acetaldehyde** and  **$\alpha$ -isobutyl-phenyl-acetaldehyde**, b.p.  $122^\circ$  (28 mm.), and  $153^\circ$  (20 mm.), respectively.  **$\beta$ -Methyl-phenyl-propylaldehyde**, b.p.  $130^\circ$  (19 mm.), is obtained from the corresponding glycidic acids by method (12) (p. 266) (*Darzens*, C.r. 139, 1214).  **$\beta$ -Phenyl-propyl-aldehyde**, *hydrocinnamaldehyde*,  $\text{PhCH}_2\text{CH}_2\text{CHO}$ , b.p.  $105^\circ$  (13 mm.), is best prepared by reducing cinnamaldehyde acetal (*Fischer*, Ber. 31, 1992). *Weston* (Am. 51, 2589) prepares it by heating cinnamaldehyde and propyl alcohol with alumina at  $330^\circ$ . It condenses with formaldehyde to  $\alpha$ -phenyl- $\beta$ -trimethylol-ethane,  $\text{PhCH}_2\cdot\text{C}(\text{CH}_2\text{OH})_3$  (*Franke*, Mo. 46, 61). For the preparation of aliphatic-aromatic aldehydes, see *Braun*, Ber. 45, 384; *Bert*, C.r. 186, 699. **3,5-Dimethyl-benzaldehyde**, mesityl-aldehyde,  $\text{Me}_2\text{C}_6\text{H}_3\text{CHO}$ , b.p.  $221^\circ$ , from mesitylene bromide (*Bamberger*, J. pr. 58, 359). **2,5-Dimethyl-benzaldehyde**, b.p.  $100^\circ$  (10 mm.), is obtained from *p*-xylyl-glyoxylic acid by method (14) (p. 266). *p*-Xylene, carbon monoxide, hydrogen chloride, etc. (method 9), give **2,4-dimethyl-benzaldehyde**, owing to atomic migration (*Francesconi*, Gazz. 32, II, 467). **2,6-Dimethyl-benzaldehyde**, m.p.  $11^\circ$ , b.p.  $226\text{--}228^\circ$  (741 mm.), is obtained from acetyl-mesitylene by the action of 2,6-dimethyl-terephthalic acid, and dimethyl-benzoyl chloride (*Lock*, J. pr. 140, 232). **2,4,6-Trimethyl-benzaldehyde** (*Chuit*, Bull. 35, 200). ***p*-Cyclohexyl-benzaldehyde**, b.p.  $160^\circ$  (12 mm.), obtained from cyclohexyl-benzene by method (9a), gives *p*-cyclohexyl-benzyl alcohol, m.p.  $41^\circ$ , and *p*-cyclohexyl-benzoic acid, m.p.  $198^\circ$ , by Cannizzaro's reaction (*Braun*, Ber. 66, 1473).

**Cuminal**, *cuminic aldehyde*, *p*-isopropyl-benzaldehyde,  $\text{Me}_2\text{CH}$  [4]- $\text{C}_6\text{H}_4$ [1]CHO, b.p.  $235^\circ$ ,  $d_{15}$  0.973, occurs, together with cymene (p. 47), in caraway oil from *Cuminum cyminum*, and in hemlock oil from *Cicuta virosa* (*Trapp*, Arch. Pharm. 231, 212). It has been prepared synthetically by *Bert* (Bull. 37, 1937) from cumenyl magnesium chloride and orthoformic ester. It has an aromatic smell. It is oxidised by dilute nitric acid to cuminic acid, but chromic acid converts it into terephthalic acid. With alcoholic potash it gives *cuminic acid* (p. 293) and *cuminyl alcohol* (p. 252). When distilled with zinc dust it gives *cymene*. A second isopropyl group can be introduced into the nucleus by treating the aldehyde with isopropyl chloride, aluminium chloride, and cuprous chloride, and **di-isopropyl-benzaldehyde**, b.p.  $147\text{--}153^\circ$ , a substance with a beautiful fragrance, is formed (Br. Pat. 293,703).

***p*-Isopropyl-phenyl-acetaldehyde**, b.p.  $243^\circ$ , is obtained from cuminic aldehyde by method (12) (p. 266) (*Chuit*, Bull. 35, 200), or from cymyl magnesium chloride and orthoformic ester (C. 1926, I, 1925).

***p*-tert.-Butyl-benzaldehyde**, b.p.  $245\text{--}246^\circ$ , is obtained from *p*-bromo-tert.-butyl-benzene, by method (9a) (*Tshitsibabin*, Bull. 43, 238).

## Functional Derivatives of Benzaldehyde

**HALOGEN COMPOUNDS, ETHERS, AND ESTERS OF BENZALDEHYDE.** Halogen derivatives of benzaldehyde are obtained by the action of phosphorus pentachloride and phosphorus pentabromide.

**Benzylidene fluoride, benzal fluoride**,  $\text{PhCHF}_2$ , b.p.  $133.5^\circ$ ,  $d_{17.5} 1.1378$ , obtained by the action of antimony trifluoride on benzylidene chloride. When nitrated it gives a mixture of the three nitro-products, the *m*-derivative predominating (*van Hove*, Bull. Belg. 1913). **Benzylidene chloride, benzal chloride**,  $\text{PhCHCl}_2$ , b.p.  $213^\circ$ ,  $d_{16} 1.295$ , is produced by the action of chlorine on boiling toluene (*Limpriht*, Ann. 139, 318; *Beilstein*, Ann. 146, 322), by the action of phosphorus pentachloride on toluene at  $170$ – $200^\circ$ , and from benzaldehyde by the action of carbonyl chloride (*Kempf*, Z. f. Ch. [2], 7, 79), or oxalyl chloride ( $\text{COCl}_2$ ) (*Staudinger*, Ber. 42, 3966). In the presence of quinoline, benzaldehyde combines with carbonyl chloride to give  $\text{PhCHCl}(\text{OCOCl})$  and  $(\text{PhCHClO})_2\text{CO}$ , m.p.  $105^\circ$  (Ger. Pat. 116,091). When benzal chloride is heated with water to  $140$ – $160^\circ$ , or with anhydrous oxalic acid to  $60$ – $70^\circ$ , it is converted into benzaldehyde. **Benzylidene bromide, benzal bromide**, b.p.  $156^\circ$  (23 mm.).

**Acetals** of aromatic aldehydes are obtained by treating them with dilute alcoholic hydrogen chloride, or with orthoformic ester or orthosilicic ester (*Helferich*, Ber. 57, 795), or by the action of sodium alkylates on aldehyde chlorides (*Fischer*, Ber. 31, 1989; *Claisen*, Ber. 40, 3903). **Benzylidene-dimethyl and -diethyl ethers**, boil at  $208^\circ$  and  $220^\circ$ , respectively. For the benzylidene compounds of polyhydric alcohols, see *Lobry de Bruyn*, Rec. 18, 150.  **$\alpha$ -Methoxy-benzyl chloride**,  $\text{PhCH}(\text{OMe})\cdot\text{Cl}$ , b.p.  $71$ – $72^\circ$  (0.1 mm.), is obtained from benzaldehyde-dimethylacetal by the action of acetyl or thionyl chloride. It decomposes at  $110^\circ$  into benzaldehyde and methyl chloride. It has a considerable tendency to enter into condensation reactions, e.g., with acetone, with which it forms benzylidene-acetone, and with acetophenone, giving benzylidene acetophenone (*Straus*, Ann. 493, 203). **Benzylidene-diacetyl ester**,  $\text{PhCH}(\text{OCOCH}_3)_2$ , m.p.  $44^\circ$ , b.p.  $220^\circ$ , is obtained by the action of lead or silver acetate on benzylidene chloride (*Bodroux*, Bull. 1899). **Diphenyl-formal peroxide**,  $\text{PhCH}(\text{OH})\text{O}\cdot\text{OCH}(\text{OH})\text{Ph}$ , m.p.  $61^\circ$ , obtained by the action of hydrogen peroxide on benzaldehyde, readily dissociates into its components (*Nef*, Ann. 298, 292). **Benzylidene**

**glycerol**,  $\text{C}_6\text{H}_5\text{CH} \begin{array}{c} \diagup \quad \diagdown \\ \text{O} \end{array} \text{C}_2\text{H}_5\text{OH}$ , m.p.  $84^\circ$ , is obtained from benzaldehyde, glycerol, and hydrogen chloride (Ger. Pat. 253,083).

**SULPHUR DERIVATIVES OF BENZALDEHYDE** (cf. thio-acetaldehydes, Vol. I, p. 245).  $\alpha$ - and  $\beta$ -Trithiobenzaldehyde, m.p.  $167^\circ$  and  $225^\circ$ , respectively (*Woerner*, Ber. 29, 159; *Hinsberg*, J. pr. 88, 800), and a polymeric thiobenzaldehyde, m.p.  $83^\circ$  (*Baumann*, Ber. 24, 1428) are known. They yield stilbene,  $\text{PhCH}=\text{CHPh}$ , on heating with copper powder. For mercaptals, such as  $\text{PhCH}(\text{SC}_2\text{H}_5)_2$ , and sulphones, such as  $\text{PhCH}(\text{SO}_2\text{C}_2\text{H}_5)_2$ , see *Posner*, Ber. 35, 2343.

**Benzaldehyde potassium bisulphite, potassium hydroxybenzyl sulphonate**,  $\text{PhCH}(\text{OH})\text{SO}_3\text{K} \cdot \frac{1}{2}\text{H}_2\text{O}$  (*Bertagnini*, Ann. 85, 186).

**Sodium benzaldehyde-sulphoxylate**,  $\text{PhCH}(\text{OH})\text{O}\cdot\text{SONa}$ , is precipitated in small flakes when benzaldehyde is added to a weakly alkaline solution of sodium hydrosulphite. The secondary salt,  $\text{PhCH}(\text{ONa})\text{O}\cdot\text{SONa}$ , forming slender needles, is more stable than the primary salt (*Bazlen*, Ber. 42, 4634).

**SELENO-BENZALDEHYDE**,  $\text{PhCHSe}$ , exists in an  $\alpha$ -form, yellow, odourless crystals, m.p.  $83^\circ$ , obtained from  $\text{C}_6\text{H}_5\text{CHO}$  and hydrogen selenide in alcohol, a  $\beta$ -form,  $(\text{PhCHSe})_n$  + 1 mol. of benzene of crystallisation, pale-yellow needles, m.p.  $205^\circ$  (free from benzene, m.p.  $218^\circ$ ), prepared like the  $\alpha$ -form, but in the presence of hydrogen chloride, and recrystallised from benzene, and in a  $\gamma$ -form, yellowish needles, m.p.  $166^\circ$ , a by-product in the above reaction. The molecular weights of these three aldehydes are unknown (*Vanino*, J. pr. 91, 116).

**NITROGEN DERIVATIVES OF BENZALDEHYDE.** **Phenyl-dinitro-methane**,  $\omega,\omega$ -dinitro-toluene,  $\text{PhCH}(\text{NO}_2)_2$ , m.p.  $79^\circ$ , is obtained by the action of nitrogen tetroxide on benzaldoxime or acetyl-benzaldoxime,  $\text{PhC}(\text{NOH})\cdot\text{COCH}_3$ . When heated to  $130^\circ$  it forms benzaldehyde, and when reduced with



aluminium amalgam it gives benzylamine and ammonia (*Ponzo*, J. pr. 65, 197; 73, 494; *Lincei* 15, II, 118; *Schimmel's Ber.* 1901). For its action on phenyl-diazonium chloride, see *Ponzo*, *Gazz.* 39, I, 625.

When ammonia at  $-20^\circ$  acts on a concentrated alcoholic solution of benzaldehyde, the first, very unstable, product is benzaldehyde-ammonia,  $(\text{PhCHOH})_2\text{NH}$ , m.p.  $45^\circ$ , which rapidly decomposes into benzaldehyde, water, and hydrobenzamide,  $(\text{PhCH})_2\text{N}_2$ , m.p.  $110^\circ$  (*Francis*, *Ber.* 42, 2216). Hence hydrobenzamide is produced whenever ammonia acts on benzaldehyde without special precautions. When heated it rearranges to *amarine* or *triphenyl-imidazoline*. When hydrogen chloride is passed into its alcoholic-benzene solution, benzylidene-imide hydrochloride,  $\text{PhCH:NH}\cdot\text{HCl}$ , is formed as crystals which melt at  $180^\circ$  (decomp.). This compound is instantaneously decomposed by water to benzaldehyde and ammonium chloride, and reacts with alcohol to give benzylidene-diethyl ether (p. 271) (*Busch*, *Ber.* 29, 2144). Benzylidene-ethylamine,  $\text{PhCH:NCH}_2\text{H}$ , m.p.  $195^\circ$ .

Benzylidene-aniline, *benzal-aniline*,  $\text{PhCH:NPh}$ , m.p.  $45^\circ$ , is obtained from benzaldehyde and aniline with the elimination of water (*Bigelow*, *Org. Synth.* 8, 22). In the presence of concentrated hydrochloric acid, aromatic aldehydes and anilines combine to give hydrochlorides of aldehyde-anilines, such as  $\text{PhCH}(\text{OH})\text{NHPh}\cdot\text{HCl}$ . These are true ammonium compounds, and some of them, especially those of the hydroxy-benzaldehydes, are fairly stable, whereas the free hydrates usually readily lose water and become benzylidene compounds (Schiff's bases) (*Dimroth*, *Ber.* 35, 934). These bases undergo hydrolysis under the influence of acids, regenerating their components, aldehydes and amines. In a few cases, Schiff's bases, like the benzaldoximes (*q.v.*), seem to occur in two isomeric forms (*Manchot*, *Ber.* 43, 3359; *Hantzsch*, *Ber.* 48, 1340; *cf.*, however, *Freundenberg*, *Stereochemie*, p. 1097). For nitration and sulphonation of benzylidene-anilines, see *Schwalbe*, *C.* 1903, I, 231. Benzylidene-aniline polymerises to a hard, brittle, resin when it is heated with 2% hydrochloric acid to  $150^\circ$  (*Ger. Pat.* 401,726). It does not give the benzoin reaction with alcoholic potassium cyanide (p. 268), but a complex condensation takes place in which hydrocyanic acid participates (*Miller*, *Ber.* 31, 2699). Benzylidene-aniline combines with alkyl-magnesium halides to form C-alkyl-benzyl-anilines,  $\text{PhCH(R)NHPh}$  (*Busch*, *Ber.* 38, 1761). When heated it partially decomposes to aniline, toluene, and *acridine* (Vol. IV) (*Reddelien*, *Ber.* 53, 355). For the condensation of benzylidene-aniline with diethyl malonate, ethyl acetoacetate, and similar compounds, see *Knoevenagel*, *Ber.* 31, 2596; *Schiff*, *Ber.* 32, 332; *Francis*, *Ber.* 36, 937.

Benzylidene-*p*-amino-dimethylaniline,  $\text{PhCH:NCH}_2\text{H}_2\text{N(CH}_3)_2$ , m.p.  $99^\circ$ , forms yellow needles. With one mol. of hydrogen chloride it gives a red, and with two mols. of hydrogen chloride, a white hydrochloride (*Moore*, *Am.* 30, 394). When benzaldehyde reacts with *o*-phenylene diamines, the first products are such compounds as benzylidene-*o*-phenylene diamine,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N:CHPh}$ , m.p.  $61^\circ$ , and dibenzylidene-*o*-phenylene diamine,  $\text{C}_6\text{H}_4(\text{N:CHPh})_2$ . These isomerise very readily to cyclic imidazole derivatives, aldehydines (p. 108) (*Hinsberg*, *Ber.* 29, 1497). The amino-benzylidene-anilines and bis-aminobenzylidene-*p*-phenylene diamines, such as  $\text{NH}_2\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\text{N:CHC}_6\text{H}_4\text{NH}_2$ , have dyeing properties similar to those of the amino-azo-compounds (p. 138), the *azomethine* group,  $-\text{CH:N}-$ , being a chromophoric group, although a much weaker one than the azo-group  $-\text{N=N}-$ . In both classes of compounds, the introduction of auxochrome groups ( $\text{NH}_2$ ,  $\text{OH}$ , etc.) causes a deepening of colour (*Möhlau*, *Ber.* 31, 2250; *C.* 1907, I, 106). For the electrolytic reduction of benzylidene bases, see *Law*, *J.* 101, 154.

Benzylidene-hydrazine, *benzal-hydrazone*,  $\text{PhCH:NNH}_2$ , m.p.  $16^\circ$ , b.p.  $140^\circ$  (14 mm.), is obtained by the action of benzaldehyde and barium monoxide on hydrazine hydrate, or by boiling benzalazine with hydrazine hydrate. It is readily converted by various methods into benzalazine. With acetic anhydride it gives benzylidene-acetylhydrazine,  $\text{PhCH:N}\cdot\text{NHCOCH}_3$ , m.p.  $134^\circ$ , which is also obtained by the action of benzaldehyde on acetyl-hydrazine (*Curtius*, *Ber.* 35, 3234).

Benzalazine,  $\text{PhCH:N}\cdot\text{N:CHPh}$ , m.p.  $93^\circ$ , is obtained from the action of hydrazine on benzaldehyde, and decomposes on heating into nitrogen and stil-

bene,  $\text{PhCH}:\text{CHPh}$ . When reduced with zinc dust and acetic acid, it loses ammonia and gives dibenzylamine (p. 257), but with sodium amalgam it is converted first into benzyl-benzylidene-hydrazine, and then into *sym*-dibenzylhydrazine (p. 259). It combines with bromine to give a tetrabromide, which readily decomposes with loss of nitrogen (*Curtius*, J. pr. 58, 372). It combines with dimethyl sulphate to give an ammonium compound,  $\text{PhCH}:\text{N}(\text{Me})\text{-(OSO}_2\text{Me)}\text{N}:\text{CHPh}$ , which decomposes when treated with water into benzaldehyde and methyl-hydrazine (*Thiele*, Ann. 376, 244). For the action of magnesium compounds on benzalazine, see *Busch*, Ber. 43, 740; for heterocyclic compounds formed from benzalazine, see *Stollé*, J. pr. 85, 386.

**Benzylidene-phenylhydrazine**, *benzal-phenylhydrazine*,  $\text{PhCH}:\text{N}:\text{NHPh}$ , m.p.  $159^\circ$  (*Vecchiotti*, Gazz. 43, II, 637), is colourless, but its alcoholic solution turns pink in light (*Stobbe*, Ber. 46, 2887). For the problem of stereoisomeric forms see *Thiele*, Ber. 31, 1249; *Lockemann*, Ber. 46, 150; *Bodfors*, Ber. 59, 666. It is reduced by sodium amalgam to *sym*-benzyl-phenylhydrazine (p. 259). When oxidised it yields partly *dibenzylidene-diphenyl-dihydrotetrazene* (p. 165), and *benzylidene-benzoyl-diphenyl-dihydrotetrazene*, and partly *benzil-osazone*, *dehydro-*



*benzylidene-phenylhydrazone*, and *tetraphenyl-dihydrotetrazene*,

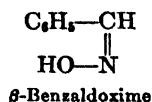
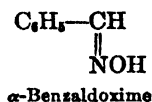


(*Bamberger*, Ber. 34, 523; *Busch*, Ber. 47, 3277). Benzaldehyde-phenylhydrazone is oxidised by perbenzoic acid (p. 298), to a compound,  $\text{C}_{11}\text{H}_{11}\text{ON}_2$ , pale yellow needles, m.p.  $201^\circ$  (decomp.), which is presumably an oxyhydrazine derivative, and may be formulated  $\text{PhCH}=\text{NO}\cdot\text{NH}\cdot\text{Ph}$ , or  $\text{PhCH}\cdot\text{N}(\text{O})\cdot\text{NHPh}$  (*Bergmann*, Ber. 56, 679).

**BENZALDOXIMES**. When free hydroxylamine acts on benzaldehyde  $\alpha$ -benzaldoxime, m.p.  $35^\circ$ , b.p.  $117^\circ$  (14 mm.), is formed. The hydrochloride of this  $\alpha$ -oxime, b.p.  $103\text{--}105^\circ$ , is only stable at low temperatures. It changes spontaneously, even at ordinary temperature, into a hydrochloride, m.p.  $63^\circ$ , from which  $\beta$ -benzaldoxime, m.p.  $132^\circ$ , is obtained by the action of cold, aqueous sodium carbonate. The same transformation of  $\alpha$ - into  $\beta$ -oxime is brought about by strong acids (*Beckmann*, Ber. 20, 2766; *Brady*, J. 123, 1783; J. 1927, 2933), metallic salts (*Hieber*, Ber. 60, 2300), or ultraviolet light (*Ciamician*, Ber. 36, 4268). When hydroxylamine hydrochloride acts on benzaldehyde dissolved in alcohol, the  $\alpha$ -oxime is formed first, but passes into the  $\beta$ -oxime (*Lindemann*, Ber. 60, 1728). Benzaldoxime is also produced when benzylamine is oxidised with permonosulphuric acid, but this reagent oxidises it further to phenyl-nitromethane (p. 256), and benzhydroxamic acid (p. 312) (*Bamberger*, Ber. 34, 2023, 2262).

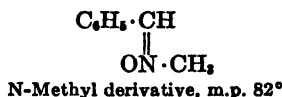
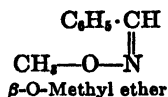
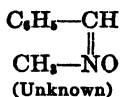
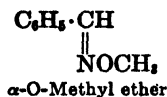
In contrast to the hydrochlorides, the  $\alpha$ -oxime is the more stable of the free oximes. The  $\beta$ -oxime passes completely into the  $\alpha$ -form under the action of heat, or by the catalytic action of mere traces of acids, or certain salts (*Taylor*, J. 1933, 1443), or certain kinds of carbon (*Freudenberg*, Stereochemie, p. 988).

The two benzaldoximes differ in reactivity, and form two distinct series of derivatives. Their isomerism is a case of *cis-trans* isomerism at the double bond between carbon and nitrogen  $\text{C}=\text{N}$ , and is to be compared with the isomerism of ethylene derivatives (Vol. I, p. 36). This was demonstrated in principle in an important paper by *Hantzsch* and *Werner* (Ber. 24, 3481), but the steric formulae suggested by them have now had to be reversed on the evidence of certain ring-closures, and of the electric moments of the O-methyl ethers (*Brady*, J. 1925, 1359; *Meisenheimer*, Ann. 446, 210; *Taylor*, J. 1933, 63):

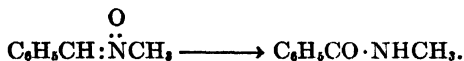


The isomeric benzaldoximes yield isomeric phenyl-urethane derivatives,  $\text{PhCH}:\text{N}\cdot\text{O}\cdot\text{CONHPh}$  with phenyl isocyanate. On methylation, the  $\alpha$ -oxime gives mainly O-methyl ether, and little of the N-methyl-derivative, and the  $\beta$ -oxime gives a little of the isomeric O-ether, and mainly the same N-methyl-derivative as the  $\alpha$ -oxime. No stereoisomeric N-methyl derivatives are known

of any aldoxime in contrast to ketoximes (*Sempler*, Ber. 51, 928; *Brady*, J. 125, 2297; 1926, 2386; *Sutton*, J. 1931, 2190). The configurations of the methyl derivatives are as follows:

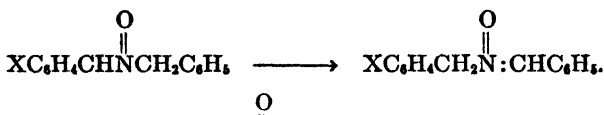


$\alpha$ -Benzaldoxime-O-methyl ether, b.p.  $196^\circ$ , is obtained from  $\alpha$ -benzaldoxime by the action of alkali and methyl iodide or dimethyl sulphate (*Ponzio*, Gazz. 37, I, 504; *Brady*, J. 1926, 2386), or diazomethane (C. 1909, II, 1754).  $\beta$ -Benzaldoxime-O-methyl ether, b.p.  $190^\circ$ , is obtained by the action of methyl iodide on the silver salt of the  $\beta$ -oxime (*Brady*, loc. cit.; C. 1913, II, 1446). N-Methyl-benzaldoxime, m.p.  $82^\circ$ , is formed, together with the isomeric O-ether, by the action of methyl iodide and sodium methylate on  $\beta$ -benzaldoxime (*Goldschmidt*, Ber. 24, 2812), or by the action of  $\beta$ -methyl-hydroxylamine hydrochloride on benzaldehyde (*Beckmann*, Ann. 365, 205). In ether solution it rearranges under the action of phosphorus pentachloride into the isomeric monomethyl-benzamide:



Benzaldoxime-O-benzyl ether,  $\text{PhCH}:\text{NOCH}_2\text{Ph}$ , is also known in two modifications, one a liquid and the other a solid, m.p.  $31^\circ$ . *p*-Chlorobenzaldoxime-*p*-chlorobenzyl ether, m.p.  $114^\circ$ , and *p*-bromobenzaldoxime-*p*-bromobenzyl ether, m.p.  $130^\circ$ , see *Schrötter*, Ber. 33, 1975. These substances decompose with difficulty, or not at all, into aldehydes and hydroxylamines.

Benzaldoxime-N-benzyl ether,  $\text{C}_6\text{H}_5\text{CH}=\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ , m.p.  $82^\circ$ , is obtained by the action of benzyl chloride on sodio-isobenzaldoxime, and also by oxidation of  $\beta$ -dibenzyl-hydroxylamine (p. 260). Ring-substituted benzaldoxime-N-benzyl ethers undergo a peculiar change under the influence of sodium ethoxide, according to the scheme (*Neubauer*, Ann. 298, 187):



N-Phenyl-benzaldoxime,  $\text{Ph}\cdot\text{CHN}\cdot\text{Ph}$ , m.p.  $109^\circ$ , is obtained by combination of benzaldehyde and N-phenyl-hydroxylamine (p. 69) (*Beckmann*, Ber. 27, 1958, Ger. Pat. 96,564). Benzaldoxime acetate,  $\text{PhCHNOCOCH}_3$ , m.p.  $15^\circ$  (*Dunstan*, Proc. 1893, 253).

Benzylidene-oxime peroxide,  $\text{Ph}\cdot\text{CH}:\ddot{\text{N}}\cdot\text{O}\cdot\text{N}:\text{CHPh}$ , m.p.  $114\text{--}116^\circ$  (decomp.), is obtained by the oxidation of benzaldoxime with sodium hypochlorite or amyl nitrite, and, together with benzo-nitrolic acid, by the action of nitrous acid on phenyl-isonitromethane. When heated in chloroform solution it undergoes a peculiar transformation to dibenzenyl-azoxime,  $\text{PhC} \begin{array}{c} \text{N} \text{---} \text{C} \cdot \text{Ph} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{N} \end{array}$

(*Wieland*, Ber. 39, 2522), but when the solution in benzene is boiled, the substance disproportionates to benzaldoxime and dibenzenyl-oxo-azoxime (*Robin*, C.r. 169, 695).

O  
||  
PhCHN·CONH<sub>2</sub>

**Benzaldoxime-carboxamide**, PhCHN·CONH<sub>2</sub>, m.p. 125°, is obtained from benzaldehyde and hydroxyl-urea (Vol. I, p. 505), and decomposes when heated into  $\alpha$ -benzaldoxime, benzonitrile, and cyanic acid (*Conduché*, Ann. Ch. Ph. [8], 13, 5).

O  
||  
PhCH=N·CH<sub>2</sub>·COOH

**Benzaldoxime-O-acetic acid**, PhCHN(OCH<sub>2</sub>COOH), m. p. 98°, and the N-derivative, PhCH=N·CH<sub>2</sub>·COOH, m.p. 183° (decomp.), are obtained by the action of chloroacetic acid on potassio-benzaldoxime. On decomposition, the O-acid gives glycolic acid, and the N-acid gives hydroxylamino-acetic acid, HO·NHCH<sub>2</sub>COOH (*Hantzsch*, Ann. 289, 286).

Isomerism similar to that shown by the benzaldoximes is also found with many of their substitution products, with ketoximes, benzil-dioximes, etc.

**Benzylidene-amino-sulphonic acid**, PhCH:NSO<sub>3</sub>H, is obtained from benzaldehyde and amino-sulphonic acid (*Krafft*, Ber. 25, 472). **Benzylidene-hydrazino-diacetic acid**, PhCH:N·N(CH<sub>2</sub>COOH)<sub>2</sub>, m.p. 123° (decomp.), is obtained by the action of hydrazine-diacetic acid and potash on benzaldehyde (*Bailey*, Am. 38, 1771).

**SUBSTITUTED BENZALDEHYDES.** Substituted benzaldehydes behave towards oxidising agents and condensing agents in the same way as benzaldehyde itself. The formation of heterocyclic compounds from *o*-nitro- and *o*-amino-benzaldehyde, is of particular interest.

**Halogen-substituted benzaldehydes** (*Blanksma*, Weekbl. 9, 862) are prepared from halogen-substituted benzylidene chlorides by the action of oxalic or sulphuric acid (*Erdmann*, Ann. 272, 148), or by oxidation of halogen-substituted cinnamic acid.

- o*-Fluorobenzaldehyde, m.p. -44.5°, b.p. 174°; oxime, m.p. 63°.
- p*-Fluorobenzaldehyde, m.p. -10.0°, b.p. 181°; oxime, m.p. 81° and 116°.
- o*-Chlorobenzaldehyde, m.p. -4°, b.p. 213°; oxime, m.p. 75°.
- m*-Chlorobenzaldehyde, m.p. 17°, b.p. 213°; oxime, m.p. 70° and 115°.
- p*-Chlorobenzaldehyde, m.p. 49°, b.p. 213°; oxime, m.p. 110°.
- o*-Bromobenzaldehyde, m.p. 21°.
- m*-Bromobenzaldehyde, b.p. 229°.
- p*-Bromobenzaldehyde, m.p. 57°.
- o*-Iodobenzaldehyde, m.p. 37°.
- m*-Iodobenzaldehyde, m.p. 57°.
- p*-Iodobenzaldehyde, m.p. 77°.

For di- and tetrachlorobenzaldehydes, see *Reich*, Bull. 21, 217; *Lock*, Ber. 69, 1527.

*o*-, *m*-, *p*-Iodoso-benzaldehyde, C<sub>6</sub>H<sub>4</sub>(IO)CHO, and *o*-, *m*-, *p*-iodoxybenzaldehyde, C<sub>6</sub>H<sub>4</sub>(IO<sub>2</sub>)(CHO), have been prepared from the iodo-chlorides (*Willgerodt*, J. pr. 86, 276; *Patterson*, J. 69, 1002).

**Nitrobenzaldehydes**, NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHO. When benzaldehyde is dissolved in a mixture of sulphuric and nitric acids, the chief product is *m*-nitrobenzaldehyde, though some *o*-nitrobenzaldehyde is formed at the same time (*Friedländer*, Ber. 14, 2803). *o*-Nitrobenzaldehyde is obtained by oxidising *o*-nitrobenzyl alcohol (Ger. Pat. 104,360), or *o*-nitrocinnamic acid, or its esters (*Einhorn*, Ber. 17, 121). It is obtained from *o*-nitrotoluene by oxidation with manganese dioxide and sulphuric acid (Ger. Pat. 179,589) or Mn(SO<sub>4</sub>)<sub>2</sub> (Ger. Pat. 175,295), or by oxidising the di-mercury compound with nitrous acid (Ger. Pat. 199,147). *o*-Nitrobenzaldehyde occurs in a stable  $\alpha$ -form, m.p. 40.9°, and in an unstable  $\beta$ -form, m.p. 37.9° (*Brady*, J. 123, 484). *p*-Nitrobenzaldehyde is obtained by oxidising *p*-nitrocinnamic acid, or from *p*-nitrotoluene in carbon disulphide by the action of chromyl chloride and water. It is also obtained by the action of lead nitrate in aqueous solution on *p*-nitrobenzyl chloride, and by the hydrolysis of *p*-nitrobenzylidene chloride with sulphuric acid. The oximes of *o*- and *p*-nitrobenzaldehyde are prepared from *o*- and *p*-nitrotoluene by the action of sodium nitrite and sodium ethoxide (Ger. Pat. 107,095; *Angeli*, Lincei 1899; *Lapworth*, Proc. 16, 108). Their acetates, C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)CH(OCOCH<sub>3</sub>)<sub>2</sub>, are ob-

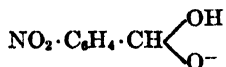
tained by oxidising a solution of *o*- or *p*-nitrotoluene, respectively, in a mixture of acetic anhydride and sulphuric acid, with chromic acid (*Thiele*, *Ann.* 311, 355).

*o*-Nitrobenzaldehyde, m.p. above; semicarbazone, m.p. 242°; hydrazone, m.p. 76°.

*m*-Nitrobenzaldehyde, m.p. 58°; semicarbazone, m.p. 246°; hydrazone, m.p. 107°.

*p*-Nitrobenzaldehyde, m.p. 107°; semicarbazone, m.p. 211°; hydrazone, m.p. 134°.

*p*- and especially *o*-Nitrobenzaldehyde dissolve in aqueous solutions of alkalis, probably attaching a hydroxyl ion, and forming the anion of a true acidic hydrate:

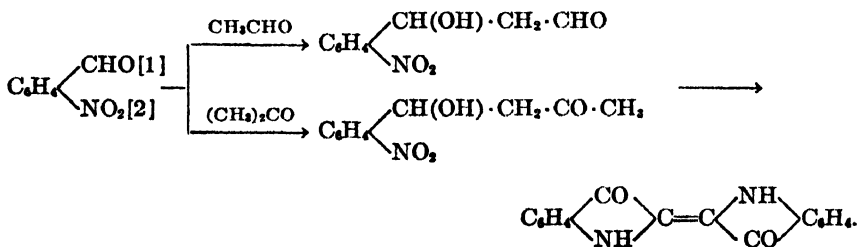


*o*- and *p*-Nitro- $\alpha$ -benzaldoximes change into the more stable  $\beta$ -aldoximes when their benzene solutions are exposed to light (*Ciamcian*, *Ber.* 36, 4268). The hydrazones of the nitrobenzaldehydes are highly coloured, and exist in two stereoisomeric forms, a red and a yellow form, the former having the *cis*- and the latter the *trans*-configuration (*Ciusa*, *Lincei* [5], 20, 578).

For the metabolism of nitrobenzaldehydes in the animal organism, see *Cohn*, *Ber.* 25, 2457.

When *o*-nitrobenzaldehyde, dissolved in indifferent solvents, is exposed to light, or when the substance is treated with an ammoniacal solution of ammonium cyanide, it rearranges completely into *o*-nitroso-benzoic acid (p. 320) (*Kühler*, *Mo.* 68, 97; *Kailan*, *Ber.* 46, 2175). In alcoholic solution, esters of *o*-nitroso-benzoic acid are formed, acetals of *o*-nitrobenzaldehyde being formed immediately. This formation of acetals, and their subsequent rearrangement into esters of *o*-nitroso-benzoic acid, is prevented by the presence of another substituent in the *o*-position to the aldehyde group. This is an example of "steric hindrance" (see p. 296) (*Bamberger*, *Ann.* 371, 319).

*o*-Nitrobenzaldehyde condenses with acetaldehyde and acetone, under the influence of dilute caustic soda, to *o*-nitro-phenyl-hydracrylic aldehyde and *o*-nitro-phenyl hydracrylic methyl ketone, which are converted by caustic soda into indigo:



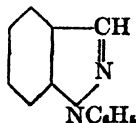
When *o*-nitrobenzaldehyde is reduced with zinc dust and alcoholic ammonia, in the presence of amyl nitrite, it yields *o*-aldehydo-nitroso-phenyl-hydroxylamine,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{N(OH)} \cdot \text{NO}$ , m.p. 52.5° (*Baudisch*, *Ber.* 45, 3429). It condenses with benzene or toluene under the influence of sulphuric acid containing traces of nitrogen trioxide, forming *acridones* (*Lehmstedt*, *Ber.* 65, 834).

5-Nitro-2-chloro-benzaldehyde,  $\text{NO}_2\text{C}_6\text{H}_3\text{ClCHO}$ , m.p. 80°, oxime, m.p. 147°. The oxime is readily converted into nitro-salicylic acid by boiling with alkali (*Meyer*, *Ber.* 28, 1253). 3-Nitro-4-bromo-benzaldehyde,  $\text{NO}_2\text{C}_6\text{H}_3\text{BrCHO}$ , m.p. 103°; oxime, m.p. 145° (*Schöpf*, *Ber.* 24, 3775). 2-Nitro-5-chloro- and -bromo-benzaldehydes, m.p. 77° and 74°, respectively, are obtained by the nitration of *m*-chloro- and *m*-bromo-benzaldehydes (*Mettler*, *Ber.* 38, 2811). 2-Nitro-4-chloro- and -bromo-benzaldehydes, m.p. 67° and 98°, are formed by treating 4-amino-2-nitro-benzaldoxime with ferric sulphate and concentrated hydrochloric or hydrobromic acids (*Sachs*, *Ber.* 37, 1861).

2,4-Dinitro-benzaldehyde,  $(\text{NO}_2)_2[2,4]\text{C}_6\text{H}_3\text{CHO}$ , m.p. 72°, is obtained by the

oxidation of 2,4-dinitro-benzylaniline or its sulphonic acid,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CH}_2\text{NHC}_6\text{H}_4\text{SO}_3\text{H}$ , with permanganate or chromic acid. Schiff's bases are first formed, of the formula  $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CH:NPh}$ , and are then decomposed by acid. The aldehyde has also been obtained from its *dimethylamino-anil*,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CH:NC}_6\text{H}_4\text{N}(\text{CH}_3)_2$ , which is prepared by the action of *p*-nitroso-dimethylaniline on 2,4-dinitro-toluene (p. 64) (Lowy, Am. 42, 849). 2,6-Dinitro-benzaldehyde, m.p.  $123^\circ$ , obtained from 2,6-dinitro-toluene as follows: 2,6-dinitrobenzyl bromide is first formed, then the anilide, which is converted into dinitrobenzylidene anilide, and then hydrolysed (Reich, Ber. 45, 804). 2,4,6-Trinitro-benzaldehyde,  $(\text{NO}_2)_3[2,4,6]\text{C}_6\text{H}_2\text{CHO}$ , m.p.  $119^\circ$ , is obtained from 2,4,6-trinitro-toluene in a similar way to the 2,4-compound (Secareanu, Ber. 64, 837). Just as *o*-nitro-benzaldehyde changes into *o*-nitroso-benzoic acid on exposure to light, the *o*,*p*-dinitro- and *sym*-trinitro-benzaldehydes readily rearrange on irradiation, into *p*-nitro-*o*-nitroso- and dinitro-*o*-nitroso-benzoic acids (Sachs, Ber. 35, 2704; 36, 959; Friedländer, Mo. 23, 543).

The phenylhydrazones of 2,6-dinitro- and 2,4,6-trinitro-benzaldehyde, but not the 2,4-derivative, rearrange into nitrated 1-phenyl-indazoles under the influence of hot alcoholic potash (Reich, Bull. 22, 107, 114):



For other condensation products of 2,4,6-trinitro-benzaldehyde see Lowy, Am. 43, 1961. 3,5-Dinitro-6-*tert*.-butyl-2,4-xylyl-1-aldehyde, *aldehyde musk*, m.p.  $112^\circ$  (Friedländer, Fortschr. Teerfarben 4, 1301).

*Hydroxylamino, nitroso, azoxy, and azo-benzaldehydes*.—When *m*- or *p*-nitrobenzaldehydes are reduced electrolytically in sulphuric acid, or by zinc dust, the first products are *aldehydo-phenyl-hydroxylamines*,  $\text{CHO}\cdot\text{C}_6\text{H}_4\text{NHOH}$ , which, however, immediately combine with unchanged nitro-aldehyde, to form *aldehydo-phenyl-nitro-N-benzaldoximes*,  $\text{NO}_2\text{C}_6\text{H}_4\text{CH=N(O)C}_6\text{H}_4\text{CHO}$ . *o*-Nitro-benzaldehyde can also be reduced to *hydroxylamino-benzaldehyde* which, however, is very unstable, and readily condenses to an internal anhydride, *anthranil*, by what may be called an internal oximisation. If the nitron formula for anthranil is adopted (p. 278), this reaction is strictly analogous to the formation of *N*-substituted oximes (nitrones) from aldehydes and *N*-substituted hydroxylamines. The nitroso-compound of *o*-hydroxylamino-benzaldehyde,  $\text{CHO}\cdot\text{C}_6\text{H}_4\text{N(NO)}\cdot\text{OH}$ , m.p.  $52.5^\circ$ , has been obtained by the reduction of *o*-nitro-benzaldehyde with zinc dust in the presence of amyl nitrite (Bamberger, Ber. 42, 2574). The same nitroso-compound is formed from anthranil by the action of nitrous acid. It forms stable salts with alkalis, while acids convert it into a mixture of diazotised *o*-amino-benzaldehyde and *o*-nitroso-benzaldehyde,  $\text{CHO}[1]\text{C}_6\text{H}_4[2]\text{NO}$ , white needles, m.p.  $110^\circ$ . See also Bamberger, Ber. 42, 2573; 43, 3321; 51, 606, where further methods of formation are given.

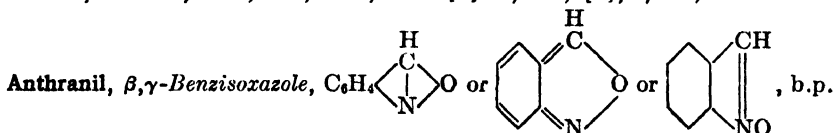
*o*-Hydroxylamino-benzaldoxime,  $\text{HONH}[2]\text{C}_6\text{H}_4\text{CH:NOH}$ , m.p.  $120^\circ$ , is formed by reduction of *o*-nitro-benzaldoxime, or by the action of hydroxylamine on anthranil. Acids reconvert it into anthranil. In air it gives the oxime,  $\text{ON}_2\cdot(\text{C}_6\text{H}_4[2]\text{CHO})_2$ , m.p.  $211^\circ$ , of 2-*azoxy*-benzaldehyde, m.p.  $119^\circ$ , which is, however, more readily obtained by reducing *o*-nitrobenzaldehyde acetal and hydrolysing the product. A peculiar reduction product of *o*-nitrobenzaldehyde  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_5$ , m.p.  $99^\circ$ , has been called *agnoto-benzaldehyde*, and the structural formula  $\text{CHO}[2]\text{C}_6\text{H}_4\text{N(OH)}\cdot\text{O}\cdot\text{N(OH)C}_6\text{H}_4[2']\text{CHO}$  has been assigned to it. It reacts as a molecular compound of *o*-nitro- and *o*-hydroxylamino-benzaldehyde. It readily breaks down into its components, of which *o*-hydroxylamino-benzaldehyde splits off water and gives anthranil, but the presence of acetic anhydride prevents water from being liberated, and *N*-acetyl-*o*-hydroxylamino-benzaldehyde, m.p.  $132^\circ$ , is formed (Bamberger, Ber. 36, 3654; 39, 4252, 4265; 51, 613).

Further reduction of *m*- and *p*-nitrobenzaldoxime-*N*-aldehydophenyl ether leads to the corresponding derivatives of azoxybenzaldoximes. These are decomposed by ferric chloride and give the *m*- and *p*-azoxybenzaldehydes,  $\text{ON}_2\cdot$

( $C_6H_5CHO$ )<sub>2</sub>, m.p. 129° and 190°, and nitroso-benzaldehydes,  $NO \cdot C_6H_5CHO$ . *p*-Azoxy-benzaldehyde is also obtained as an aniline compound,  $ON_2(C_6H_5CH:NPh)_2$ , by the action of potash on *p*-nitro-benzyl-aniline,  $NO_2C_6H_4CH_2NHPh$ . *p*-Nitroso-benzaldehyde combines with aniline to give the anil of phenyl-azo-*p*-benzaldehyde,  $PhN:NC_6H_4CHO$ , m.p. 120°. The acetal of this compound, together with the acetal of *p*-azobenzaldehyde,  $CHO \cdot C_6H_4N:NC_6H_4CHO$ , m.p. 238°, is also formed when a mixture of nitrobenzene and *p*-nitro-benzaldehyde acetal is reduced. *o*- and *m*-Azobenzaldehyde acetal, m.p. 144° and 150°, are obtained from the corresponding nitrobenzaldehyde acetals by reduction with zinc dust and soda. *o*-Azobenzaldehyde acetal is hydrolysed by dilute sulphuric

acid to  $\gamma$ -hydroxy- $\beta$ -phenyl-indazole,  $C_6H_5 \begin{array}{c} C(OH) \\ \diagup \quad \diagdown \\ N \end{array} NC_6H_5$  (Athey, Ber. 35,

2434; 36, 793; Am. Ch. J. 28, 34; Am. 24, 1052, 1060; Human, Ber. 36, 3469; Freundler, C.r. 134, 1359; 135, 1116; Bull. [3] 31, 449; [4], 1, 234).



99° (13 mm.) (Bamberger, Ber. 42, 1647), is an oil with a characteristic odour, volatile in steam. It is formed: (1) by careful reduction of *o*-nitrobenzaldehyde with tin and acetic acid, or with ferrous salts and ammonia. *o*-Hydroxylamino-benzaldehyde would be expected to be formed, but is immediately dehydrated. Its formation from *o*-hydroxylamino-benzaldehyde by the action of acids is explained similarly (p. 277). (2) When *o*-nitrosobenzyl alcohol is boiled with water anthranil is formed. (3) It is also obtained by treating di-mercurio-*o*-nitrotoluene with concentrated hydrochloric acid. (4) It is also formed from *o*-azido-benzaldehyde (page 279). (5) Oxidation of *o*-amino-benzaldehyde with permanganosulphuric acid gives anthranil. Reactions (2) and (3) involve an internal oxidation-reduction of the N- and C-atoms in the *o*-position (p. 60). Reaction (3) starts from the oxidation levels "nitro" and "methane," and (2) from "nitroso" and "methylol," and both lead to "hydroxylamino" and "aldehyde." The aldehyde nature of anthranil is proved by its re-conversion into hydroxylamino-benzaldehyde by hydroxylamine, and by its conversion into nitroso-*o*-hydroxylamino-benzaldehyde by nitrous acid. The final stage of the oxidation and reduction of N and C is not yet attained in anthranil. This step is brought about by the action of caustic alkalis, which convert anthranil into anthranilic acid (p. 321), or of acetic anhydride, which gives the internal anhydride of aceto-anthranilic acid (p. 322). On the strength of these two transformations, anthranil was for some time regarded as an internal anhydride of anthranilic

acid, and formulated as a lactam,  $C_6H_5 \begin{array}{c} CO \\ | \\ NH \end{array}$ ; hence the name anthranil. This

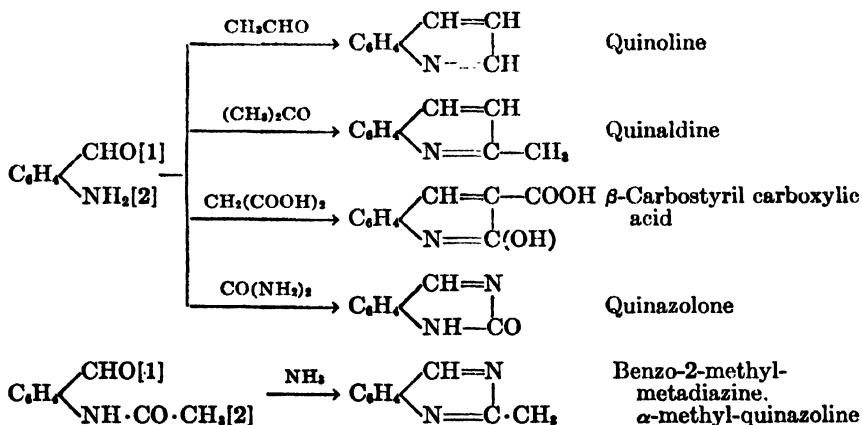
formula, however, would imply that N and C exchange oxidation levels in the opposite direction in the conversion of anthranil into *o*-hydroxylamino-benzaldehyde, and this is quite contrary to experience with the Beckmann transformation of oximes, and other reactions. Indeed anthranilic acid, on removal of water, is not converted into anthranil, but gives di-anthranilide (p. 324), a dimolecular anhydride of totally different properties from anthranil. Other facts which support the formulation of anthranil as an internal anhydride of *o*-hydroxylamino-benzaldehyde are: the ease of reduction to *o*-amino-benzaldehyde, which would be inconceivable with a derivative of anthranilic acid, and, especially, the close analogy of the reduction of *o*-nitro-acetophenone to C-methyl-anthranil (p. 286); the latter could not be formulated as a lactam, whilst its constitutional analogy with anthranil is proved by the absorption spectra of the two compounds (Scheiber, Ber. 44, 2409). A further analogy is furnished by the transformation of *o*-hydroxylamino-phenyl-glyoxylic acid into anthroxanic acid (p. 426), which is also a reaction which occurs spontaneously, and the course of which is known.

Anthranil combines with mercuric chloride to give a characteristic double compound,  $C_7H_5ONHgCl_2$ , b.p. 178°, and with chlorine to give a dichloride, m.p.





benzaldehyde combines readily with compounds containing a  $\text{CH}_2\text{CO}$ -group, especially in the presence of dilute sodium hydroxide. Water is eliminated and quinoline derivatives formed. *o*-Aminobenzaldehyde combines with acetaldehyde to give *quinoline*; with acetone it gives *quinaldine*; with malonic acid it gives  $\beta$ -carbostyryl-carboxylic acid; and with urea it gives *quinazalone* (Eliasberg, Ber. 26, 1752; Gabriel, Ber. 28, 1037). Alcoholic ammonia converts the acyl-*o*-aminobenzaldehydes into quinazolines:



For the condensation of *o*-aminobenzaldehyde to *anhydro-o*-aminobenzaldehyde,  $(\text{C}_7\text{H}_7\text{N})_2$ , through the agency of zinc chloride, see Posner, Ber. 31, 658.

Benzaldehyde-*m*-sulphonic acid,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4\text{CHO}$ , forms white deliquescent crystals (Kafka, Ber. 24, 791). Benzaldehyde-*o*-sulphonic acid is obtained by the action of sodium sulphite on *o*-chlorobenzaldehyde, and by the oxidation of *o,o*-stilbene-disulphonic acid. Its chloride, m.p.  $115^\circ$ , gives *saccharin* (p. 333) when treated with ammonia and subsequently oxidised by atmospheric oxygen (Ger. Pats. 94,947, 115,410, and 119,163). In order to account for the fact that the chloride is stable towards phosphorus pentachloride, the formula

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CHCl} \\ \text{SO}_2 \end{array} \text{O}$  has been suggested for it (Goldberger, Mo. 37, 125). Benzaldehyde-mono- and -disulphonic acids are also produced when toluene-sulphonic acids are oxidised with manganese dioxide in fuming sulphuric acid (Ger. Pat. 154,528).

### 3. Aromatic Monoketones

The oxidation products of secondary phenyl paraffin alcohols are *mixed ketones*, of which the CO-group is linked on the one hand to an aromatic and on the other to an aliphatic hydrocarbon residue. Ketones in which the CO-group links two aromatic hydrocarbon residues are also known, such as benzophenone or diphenyl ketone. These will be dealt with later, after the corresponding hydrocarbons of the diphenyl-methane type.

**Methods of preparation.**—The mixed aromatic-aliphatic ketones are usually prepared by the same reactions as those giving rise to aliphatic ketones (Vol. I, p. 256). They are obtained:

1. From ethyl-benzene, and similar benzene homologues with two or more carbon atoms in the side-chain, by catalytic oxidation (Fr. Pat. 646,087; Ger. Pat. 522,255; U. S. Pat. 1,813,606).

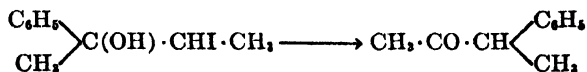
2. From secondary alcohols, such as phenyl-methyl carbinol, by

oxidation, or by an exchange of oxidation levels with an aldehyde or ketone (*Ponndorf*, *Z. angew.* **39**, 138).

*3a.* From di-secondary- and secondary-tertiary-phenyl-ethylene glycols and ethylene oxides, by heating with dilute acid or alone (*Fourneau*, *C.r.* **141**, 662; *Tiffeneau*, *Ann. ch. ph.* [8], **10**, 322).



*3b.* By treating the iodohydrins of some olefine-benzenes with silver nitrate or mercuric oxide, when a migration of the phenyl group takes place (*cf.* p. 265):



*3c.* By reduction of unsaturated ketones, such as benzylidene acetone,  $\text{PhCH}:\text{CHCOCH}_3$ .

4. By the action of sulphuric acid on phenyl-acetylene:

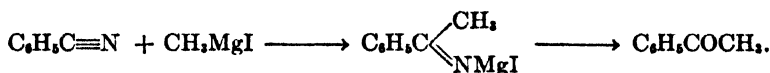


*Nuclear syntheses.*

*5a.* By distilling a mixture of the calcium salts of an aromatic and an aliphatic acid (*cf. Senderens*, *C.r.* **150**, 111). *5b.* By passing the vapours of aromatic mono- and di-carboxylic acids, or of phenyl-fatty acids, mixed with an excess of the vapour of an aliphatic acid, over manganous oxide or thoria, heated to 460° (*Lakomkin*, *C.* **1930**, **II**, 3398; *Fr. Pat.* 698,230).

6. By the action of zinc alkyls or mixed zinc organo-compounds on acid chlorides (*Freund*, *Ann.* **118**, 20; *Mauthner*, *J. pr.* **103**, 391).

7. By the action of alkyl magnesium iodides on aromatic nitriles, addition compounds are obtained, which are decomposed by mineral acids with the formation of aromatic ketones (*Blaise*, *C.r.* **133**, 217):



Phenyl cyanate,  $\text{PhCNO}$ , gives ketoximes with alkyl magnesium halides (*Wieland*, *Ber.* **40**, 1672).

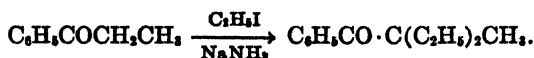
8. By the action of aliphatic acid chlorides or anhydrides on benzene hydrocarbons in the presence of aluminium chloride or ferric chloride. Addition compounds of the acid chloride and the metallic chloride, *e.g.*,  $(\text{AcCl})\text{AlCl}_3$ , are first formed, and then these react with the hydrocarbons (*Böseseken*, *Rec.* **20**, 102; *Perrier*, *Ber.* **33**, 815; *Kronberg*, *J. pr.* **61**, 494; *Skraup*, *Ber.* **57**, 1294; *Unger*, *Ann.* **504**, 267). A mixture of a fatty acid and acid anhydride may be used instead of the chloride.

9. By heating aryl-glycidic acids (p. 420), which are easily synthesised by condensing aromatic aldehydes or ketones with  $\alpha$ -chloropropionic ester and sodium ethoxide (*Darzens*, *C.r.* **142**, 214):



10. By the action of diazomethane on aldehydes (*Schlatterbeck*, *Ber.* **40**, 479).

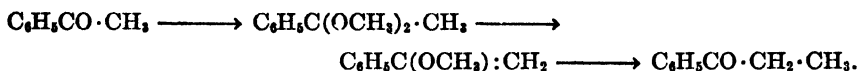
11. The hydrogen atoms adjoining the carbonyl group in alkyl-phenyl ketones can be replaced by alkyl groups by the action of sodamide and alkyl halides (*Haller*, *C.r.* **148**, 70; **149**, 5; *Dumesnil*, *Ann. chimie*, [9] **8**, 70):



12. By decomposing  $\beta$ -ketocarboxylic acids, *e.g.*, mono- and di-alkyl-benzoyl-acetic acids (*Baeyer, Perkin*, Ber. 16, 2131), with alcoholic potash, or from tertiary phenyl-carbinols,  $\text{Ar} \cdot \text{C}(\text{R})(\text{OH})\text{Alk}$ , which decompose on distillation *in vacuo*, at higher temperatures, into hydrocarbons,  $\text{Alk} \cdot \text{H}$ , and ketones,  $\text{Ar} \cdot \text{CO} \cdot \text{R}$  (*Grignard*, C.r. 182, 299).

13. Arylated-aliphatic ketones,  $\text{Ar} \cdot \text{CHR} \cdot \text{CO} \cdot \text{R}$ , are formed by the action of concentrated sulphuric acid on disubstituted aromatic aldehydes,  $\text{Ar} \cdot \text{C}(\text{R})_2 \cdot \text{CHO}$ , one alkyl group migrating. Thus, phenyl-dimethyl-acetaldehyde gives 2-phenyl-butan-3-one (*Orechov*, C.r. 182, 67).

14. Finally, acylated benzene hydrocarbons are formed by a rearrangement which the alkyl ethers of phenyl-olefine alcohols undergo on heating. Since the latter are obtained by distilling acetophenone ortho-ethers, this method makes it possible to build up homologous acyl-benzenes from acetophenone (*Claisen*, Ber. 29, 2931):



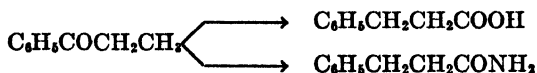
Acetophenone and higher ketones are found in the heavy oil in the distillation of coal-tar (*Weissgerber*, Ber. 36, 654).

*Properties and reactions.*—The mixed aromatic-aliphatic ketones are colourless liquids, insoluble in water. Some of them possess a pleasant smell.

1. On reduction they give secondary alcohols or alkyl-benzenes (*Darzens*, C.r. 139, 868). For the catalytic reduction of these compounds with formic acid, see *Mailhe*, Bull. 21, 61.

2. On oxidation, (a) with chromic acid mixture, the ketones  $\text{PhCOR}$  split off the alkyl group, and give benzoic acid; (b) with potassium permanganate,  $\alpha$ -ketocarboxylic acids are formed (*Claus*, J. pr. 41, 396; 46, 474; *Feith*, Ber. 24, 3543).

3. When phenyl-alkyl ketones are heated with yellow ammonium sulphide, a rather surprising reaction takes place, *viz.*, the formation of acids and amides with the same number of carbon atoms (*Willgerodt*, J. pr. 81, 74, 382):



With increasing number of carbon atoms in the side-chain, the yield of carboxylic acid decreases, there being no yield at all in the case of phenyl-heptyl ketone.

4. The mixed ketones are converted into benzene sulphonic acids by heating with sulphuric acid (*Krekeler*, Ber. 19, 2623).

5. Those ketones in which the CO-group is attached to the ring do not form bisulphite compounds. 6. Phenyl-alkyl ketones seem to form only one oxime with hydroxylamine (*cf.* benzophenone), while benzaldehyde gives two. 7. They give phenylhydrazones with phenylhydrazine. 8. The aryl-methyl ketones, especially, form crystalline compounds with phosphoric and arsenic acids, which form the hydrocarbons on heating, the carbonyl group being split off (*Klages*, Ber. 32, 1549; 35, 2313). 9. When trialkyl-acetophenones in benzene solution are heated with sodamide, they decompose into benzene and trialkyl-acetamides (*Haller*, C.r. 148, 127; 149, 5; Ann. ch. ph. [9], 1, 5):



10. On reduction with amalgamated zinc and hydrochloric acid (*Clemmensen*, Ber. 47, 681), or by hydrogenation at 260–280° under pressure (*Ipatiev*,

C. 1930 I, 2081), alkyl-benzenes are obtained. 11. The hydrogen atoms of the acyl-group can be replaced, all or in part, by chlorine, by the action of hypochlorites (Gray, J. 53, 3494). 12. When acted upon by diazomethane, these ketones are converted partially into derivatives of ethylene oxide,  $\text{Ar} \cdot \text{C}(\text{Alk}) \cdot \text{CH}_2$ ,

and partly, with the migration of the phenyl group, into aralkyl-alkyl-ketones, which then react with more diazomethane to form alkylene oxides (Mosetti, Mo. 53, 427). 13. With cyanacetic ester and ammonia, cyclo-dicyano-glutarimides are formed, e.g.,  $\beta$ -benzyl- $\beta$ -methyl- $\alpha, \alpha'$ -dicyano-glutarimide from benzyl-methyl-ketone (Guareschi, Gazz. 48, II, 83). For the transformations of aromatic ketones in the animal body see Tierfelder, Z. physiol. Ch. 131, 380.

**ACETOPHENONE**, *phenyl-methyl ketone*,  $\text{C}_6\text{H}_5\text{COCH}_3$ , m.p.  $20^\circ$ , b.p.  $202^\circ$ , crystallises in large leaflets. It is used as a perfume and as a soporific, under the name of *hypnone*. It is the chief constituent of the essential oil of *Stillingia latifolia*, and has been found in *castoreum* (Walbaum, J. pr. 117, 225). It is obtained by the general methods given above: (1) from phenyl-methyl carbinol; (2) from phenyl-acetylene; (3) from calcium benzoate and acetate; (4) from benzoyl chloride and zinc methyl; (5) from benzene and acetyl chloride in the presence of aluminium chloride or ferric chloride; (6) from benzaldehyde and diazomethane; (7) from benzoyl-acetoacetic ester,  $\text{C}_6\text{H}_5\text{CO} \cdot \text{CH}(\text{COCH}_3) \cdot \text{COOC}_2\text{H}_5$ , and benzoyl-acetic ester; (8) from ethyl-benzene, (iso-)propyl-benzene, etc., by catalytic oxidation (Senseman, Ind. Eng. 25, 1286). Reactions (3) and (5) are used as methods of preparation.

Acetophenone is readily reduced to phenyl-methyl carbinol, or, catalytically by means of platinum or iron, to ethyl-cyclohexanone (Fallebin, Ann. chim. [10], 4, 156). It is oxidised by chromic acid to benzoic acid, and by potassium permanganate to phenyl-glyoxylic acid.

Like acetone, acetophenone has been used in many nuclear-synthetic reactions. A few of the simpler ones are: its condensation to *dyppnone*,  $\text{PhCOCH}:\text{C}(\text{CH}_3)_2$  (Ph) (Konowalow, C. 1903, I, 521), and to 1,3,5-triphenyl-benzene (Gastaldi, Gazz. 45, II, 251), two substances related to acetophenone in the same way as mesityl oxide and mesitylene are to acetone. Acetophenone condenses with benzaldehyde in various proportions, giving rise to benzylidene-acetophenone, benzylidene-diacetophenone, and dibenzylidene-triacetophenone (Kostanecki, Ber. 29, 1488). Acetophenone reacts with chloroformic ester and sodamide both as a ketone and in an enol form. In the first case, two hydrogen atoms of the methyl group are replaced by the carbethoxy group, and benzoyl-malonic ester is formed, while in the second case, the hydroxyl hydrogen and one hydrogen atom of the methyl group are replaced by carbethoxy and  $\beta$ -carbethoxy-hydroxycinnamic ester is formed (Haller, Ann. chim. [10], 1, 275).

Acetophenone combines with hydrogen cyanide to form the nitrile of  $\alpha$ -phenyllactic acid. At high temperatures chlorine substitutes in the methyl group, but phosphorus pentachloride replaces oxygen, and forms acetophenone chloride (Ladenburg, Ann. 217, 105). With amyl nitrite and sodium ethoxide, acetophenone forms *isonitroso-acetophenone*, which will be dealt with later together with phenyl-glyoxal. With sodium ethoxide alone, a mixture of *o*-methyl-diphenyl-benzene and 4-(or 6-)benzoyl-3,5-diphenyl-toluene is produced (Gastaldi, Gazz. 50, 71). Acetophenone reacts with ammonia, like the higher aliphatic ketones, to form acetophenone ammonia,  $(\text{PhMeC})_2\text{N}_3$ , m.p.  $115^\circ$  (Thomae, Arch. Pharm. 244, 653).

*Ortho-ethers of acetophenone*, such as acetophenone-*o*-ethyl ether, acetophenone acetal,  $\text{PhC}(\text{OEt})_2\text{Me}$ , b.p.  $107^\circ$  (17 mm.), are obtained by action of orthoformic esters on acetophenone (Claisen, Ber. 40, 3908). When heated at ordinary pressure, or, preferably, when treated with acid chlorides and pyridine (Claisen, Ber. 31, 1019), they lose alcohol, giving alkyl ethers of phenyl-olefine alcohols. With

aniline they form anils, such as acetophenone-anil,  $\text{PhC}:(\text{NPh})\text{Me}$ , m.p.  $41^\circ$ , b.p.  $310^\circ$ . Acetophenone-ethyl mercaptol,  $\text{PhC}(\text{SEt})_2\text{Me}$ , is oxidised by permanganate in the cold to a disulphone,  $\text{PhC}(\text{SO}_2\text{Et})_2\text{Me}$ , m.p.  $120^\circ$  (Posner, Ber. 35, 2343).

**Acetophenone oxime**,  $\text{C}_6\text{H}_5\text{C}:(\text{N}\cdot\text{OH})\text{CH}_3$ , m.p.  $59^\circ$ , is known in only one modification (Hantzsch, Ber. 24, 3482). In 1887, Beckmann (Ber. 20, 2580; Goldschmidt, Ber. 23, 2746) discovered the remarkable rearrangement by which acetophenone oxime in acetic acid solution is converted into acetanilide,  $\text{Ph}\cdot\text{NHCOCH}_3$ , under the action of concentrated sulphuric or hydrochloric acid. This reaction is shown by many ketoximes. It is used to determine the position of the double bonds in higher olefine-carboxylic acids (Vol. I, p. 337), and to break down cyclic ketones. When hydroxylamine acts on cinnamic acid, acetophenone is formed together with  $\beta$ -amino-hydrocinnamic acid (Posner, Ann. 389, 118). **Acetophenone phenylhydrazone**, m.p.  $105^\circ$ .

**HOMOLOGUES OF ACETOPHENONE.** Numerous homologues of acetophenone are known. They may be divided into two groups as follows. (A) *Acylated benzenes*, or ketones whose CO-group is attached directly to the ring, and (B) *phenylated aliphatic ketones*, of which the CO-group is not directly linked to the ring.

(A) **ACYLATED BENZENES** have been made particularly by the general methods 5a, 7, 11, 12, and 13 (p. 281).

| Benzoylated paraffins                     | Formula                                                                          | M.p.       | B.p.                 |
|-------------------------------------------|----------------------------------------------------------------------------------|------------|----------------------|
| Propiophenone <sup>a</sup>                | $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$                                   | $21^\circ$ | $210^\circ$          |
| Butyrophenone                             | $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_2\text{CH}_3$                        | $11^\circ$ | $231^\circ$          |
| Isobutyrophenone <sup>b</sup>             | $\text{C}_6\text{H}_5\text{COCH}(\text{CH}_3)_2$                                 | ...        | $222^\circ$          |
| Valerophenone                             | $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_3\text{CH}_3$                        | ...        | $248^\circ$          |
| Isovalerophenone                          | $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}(\text{CH}_3)_2$                      | ...        | $235^\circ$          |
| Tert.-butyl-phenyl ketone <sup>c</sup>    | $\text{C}_6\text{H}_5\text{COC}(\text{CH}_3)_3$                                  | ...        | $110^\circ$          |
| Capronophenone <sup>d</sup>               | $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_4\text{CH}_3$                        | $27^\circ$ | $133^\circ$ (14 mm.) |
| Isoamyl-phenyl ketone                     | $\text{C}_6\text{H}_5\text{COCH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)_2$ | ...        | $255^\circ$          |
| Diethyl-acetophenone                      | $\text{C}_6\text{H}_5\text{COCH}(\text{C}_2\text{H}_5)_2$                        | ...        | $242^\circ$          |
| Ethyl-dimethyl-acetophenone <sup>e</sup>  | $\text{C}_6\text{H}_5\text{COC}(\text{CH}_3)_2\text{C}_2\text{H}_5$              | ...        | $112^\circ$ (10 mm.) |
| Hexyl-phenyl ketone                       | $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_5\text{CH}_3$                        | $17^\circ$ | $155^\circ$ (15 mm.) |
| Propyl-dimethyl-acetophenone <sup>f</sup> | $\text{C}_6\text{H}_5\text{COC}(\text{CH}_3)_2\text{C}_3\text{H}_7$              | ...        | $122^\circ$ (10 mm.) |
| Triethyl-acetophenone <sup>g</sup>        | $\text{C}_6\text{H}_5\text{COC}(\text{C}_2\text{H}_5)_3$                         | ...        | $145^\circ$ (10 mm.) |
| Lauroyl-benzene <sup>h</sup>              | $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_{10}\text{CH}_3$                     | $47^\circ$ |                      |
| Palmitoyl-benzene                         | $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_{14}\text{CH}_3$                     | $59^\circ$ |                      |

<sup>a</sup> Kishner, C. 1913, II, 2129. <sup>b</sup> Auwers, J. pr. 82, 132. <sup>c</sup> Nef, Ber. 45; 2772.

<sup>d</sup> Schroeter, Ber. 40, 1601. <sup>e</sup> Haller, C.r. 148, 70. <sup>f</sup> Kipping, J. 67, 502.

For benzoyl-cyclopropane and benzoyl-cyclobutane, see Vol. II, p. 25 and p. 33; the latter can be prepared from  $\gamma$ -chlorobutyrophenone by the action of potassium cyanide (Allen, Canad. J. 9, 159).

*Nuclear-acylated alkyl-benzenes:*

**p-Acetyl-toluene**,  $\text{CH}_3\text{CO}[4]\cdot\text{C}_6\text{H}_4[1]\cdot\text{CH}_3$ , m.p.  $28^\circ$ , b.p.  $224^\circ$ .

**1-Acetyl-3,4-(o)-xylene**, b.p.  $250^\circ$ .

**1-Acetyl-2,4-(m)-xylene**, b.p.  $228^\circ$ .

**Acetyl-p-xylene**, b.p.  $224^\circ$ .

**Acetyl-mesitylene**, b.p.  $235^\circ$ .

**1-Acetyl-2,3,5-durene**, m.p.  $73^\circ$ , b.p.  $260^\circ$ .

**2-Acetyl-cymene, 2-methyl-5-isopropyl-acetophenone**, b.p. 124–125° (12 mm.) (*Allen*, *Org. Synth.* 14, 1).

**Diisopropyl-acetophenone**, b.p. 145–150° (13 mm.), possesses an odour reminiscent of musk (*Ger. Pat.* 502,333).

*p*-Acetyl-toluene has been obtained by the action of concentrated nitric acid on cymene (p. 47), and acetyl-3,4-(*o*)-xylene has been obtained by the action of concentrated sulphuric acid on camphor or fenchone (*Weygand*, *Ber.* 68, 1825).

(B) **PHENYLATED KETONES** have been prepared by methods 3, 5a, 6, 7, 9, 11, and 12 (p. 281):

**Phenyl-acetone**, benzyl-methyl-ketone,  $C_6H_5CH_2CO \cdot CH_3$ , m.p. 27°, b.p. 216°.

**Benzyl-ethyl-ketone**,  $C_6H_5CH_2 \cdot CO \cdot CH_2CH_3$ , b.p. 230°.

**Benzyl-acetone**,  $C_6H_5CH_2 \cdot CH_2 \cdot CO \cdot CH_3$ , b.p. 235°.

**Methyl-phenyl-acetone**,  $C_6H_5CH(CH_3) \cdot COCH_3$ , b.p. 211°.

For higher benzyl-alkyl-ketones of the type  $Ar \cdot CHR \cdot COR$ , see *Jullien*, *Bull.* [5], 3, 1347.

**Benzyl-propyl-ketone**,  $C_6H_5CH_2COCH_2CH_2CH_3$ , b.p. 244°, has been obtained from benzyl cyanide and propyl-magnesium iodide, *etc.* (*Blaise*, *C.r.* 133, 217; *Senderens*, *C.r.* 150, 1336).

**Benzyl-methyl-ethyl ketone**,  $PhCH_2 \cdot CH_2 \cdot COC_2H_5$ , b.p. 251°, is obtained by reduction of  $\alpha$ -benzylidene-methyl-ethyl ketone, or by distilling calcium hydrocinnamate and propionate (*Harries*, *Ber.* 35, 971).

**Methyl-( $\beta$ -*p*-tolyl)-propyl ketone**, *curcumone*,  $CH_3COCH_2CHCH_3 \cdot C_7H_7(p)$ , b.p. 130.5° (11 mm.), an optically active substance, is obtained by boiling curcuma oil with potash. Its racemic form has been prepared synthetically by *Rupe* (*Helv.* 7, 654) from *p*-methyl-acetophenone.

**Methyl-( $\beta$ -benzyl)-isopropyl ketone**,  $CH_3COCH(CH_3)CH_2C_7H_7$ , b.p. 127–128° (8 mm.), is obtained from  $\alpha$ -methyl- $\gamma$ -phenyl-butyryl chloride by the action of zinc methyl (*Rupe*, *Helv.* 14, 687).

**Methyl-( $\beta$ -phenyl)-isobutyl ketone**,  $CH_3COCH_2C(CH_3)_2C_6H_5$ , b.p. 252° (*Hoffmann*, *Am.* 51, 2542). **Pseudocumyl acetone**,  $CH_3COCH_2[1]C_6H_4[2,4,5](CH_3)_3$ , m.p. 69–70°, is found in crude wood-tar (*Holmberg*, *Sv. kem.* 40, 304).

**Methyl-( $\gamma$ -*p*-tolyl)butyl ketone**, *homocurcumone*,  $CH_3COCH_2CH_2CHCH_3 \cdot C_7H_7(p)$ , b.p. 141° (11 mm.), has been prepared synthetically by a method similar to curcumone, from the corresponding ketone (*Rupe*, *Helv.* 9, 992). ***sym*-Tetra-phenyl-acetone**,  $(C_6H_5)_2CHCOCH(C_6H_5)_2$ , m.p. 134° is produced by the action of sodium on dissolved, or molten, diphenyl-acetic ester (*Vorländer*, *Ber.* 56, 1125).

For the action of diazomethane on phenylated aliphatic ketones, see *Mosettig*, *Mo.* 53/54, 427.

**SUBSTITUTED ACETOPHENONES. HALOGEN-SUBSTITUTED ACETOPHENONES.** Acetophenones halogenated in the methyl group will be dealt with in connection with the corresponding oxygenated compounds; *cf.* *benzoyl carbinol*, p. 403, *phenyl-glyoxal*, p. 407, and *phenyl-glyoxylic acid*, p. 422. *p*-Halogeno-acetophenones, such as  $Cl \cdot C_6H_4 \cdot COCH_3$ , are obtained by the action of halogeno-benzenes on acetyl chloride in the presence of aluminium chloride (*Gauthier*, *Bull.* [2], 43, 602; *Collet*, *Bull.* [3], 21, 68; *Schweitzer*, *Ber.* 24, 997; *Schoepff*, *Ber.* 24, 3766; *Bösesen*, *Rec.* 27, 5).

(18 mm.).

For iodide-chlorides and iodoso-compounds of *p*-iodo-acetophenone, and other ketones, see *Werner*, *J.* 89, 1625; *Caldwell*, *J.* 91, 240; *Willgerodt*, *Ann.* 389, 292.

**Nitro-acetophenones.**—When the nitration of acetophenone is carried out at low temperatures, *m*-nitro-acetophenone is the chief product (m.p. 77°). Some *o*-nitro-acetophenone and a very small amount of the *p*-compound are formed at the same time (*Morgan*, *Ind. Eng.* 55, 29). With rising temperature, the yield of *m*-nitro-acetophenone decreases through the formation of its *iso*-nitroso-derivative (*Ar. Pharm.* 240, 1). The three isomeric nitro-acetophenones,  $NO_2 \cdot C_6H_4 \cdot$

$\text{CO}\cdot\text{CH}_3$ , are obtained from the three *nitrobenzoyl-acetoacetic esters* (*q.v.*) (*Gevekoht*, Ann. 221, 326; *Krermack*, J. 1929, 814). *p*-Nitro-acetophenone is also formed by the action of concentrated sulphuric acid on *p*-nitrophenyl-propionic acid (p. 480), by the hydration of the *nitro-phenyl-acetylene* first produced (*cf.* method 4, p. 281) (*Drewson*, Ann. 212, 160).

*o*-Nitro-acetophenone, b.p.  $159^\circ$  (16 mm.); oxime, m.p.  $115^\circ$ .

*m*-Nitro-acetophenone, m.p.  $81^\circ$ ; oxime, m.p.  $131^\circ$ .

*p*-Nitro-acetophenone, m.p.  $80^\circ$ , oxime, m.p.  $172^\circ$ .

*o*-Nitro-acetophenone oxime is obtained by the action of amyl nitrite and sodium ethylate on *o*-nitro-ethylbenzene,  $\text{NO}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_5$  (*cf.* nitrobenzaloximes, p. 276) (*Ger. Pat.* 109,663).

*m*-Dinitro-acetophenone, m.p.  $83^\circ$ , is prepared by the action of sulphuric acid on dinitrobenzoyl-acetoacetic ester (*Berend*, J. pr. 65, 290). Dinitro-*tert*-butyl-acetyl-*m*-xylene, *keto-musk*,  $\text{C}_6(\text{CH}_3)_2[1,3](\text{COCH}_3)[2]\text{C}_6\text{H}_4[5](\text{NO}_2)_2[4,6]$ , m.p.  $134^\circ$  (*Tshitshibabin*, Bull. 51, 1436).

By gentle reduction with zinc and ammonium chloride, or tin and acetic acid, *o*-nitro-acetophenone is converted into *o*-hydroxylamino-acetophenone anhydride,

or *C*-methyl-anthranil,  $\text{C}_6\text{H}_4\left\langle \begin{array}{c} \text{C}\cdot\text{CH}_3 \\ | \\ \text{N} \end{array} \right\rangle \text{O}$ , b.p.  $111^\circ$  (10 mm.), a colourless oil,

which is readily volatile in steam. Like anthranil, it forms a double compound with mercuric chloride. On further reduction it gives amino-acetophenone, and on heating under ordinary pressure, it rearranges to *indoxyl* and *indigo* (*Gevekoht*, Ann. 221, 326; *Bamberger*, Ber. 36, 1611). For *m*-hydroxylamino-, azoxy-, and azo-acetophenones, see *Bamberger*, Ber. 36, 1618, and *Elbs*, Z. Elektroch. 9, 428.

**Amino-acetophenones**, *o*-, *m*-, and *p*-amino-acetophenones,  $\text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3$ , have been obtained by reducing nitro-acetophenones (*Gevekoht*, Ann. 221, 326; *Nord*, Ber. 52, 1705); the *o*-compound has also been obtained by boiling *o*-amino-phenylpropionic acid with water, by treating *o*-amino-phenylacetylene with concentrated sulphuric acid (*Baeyer*, Ber. 15, 2153; 17, 964), and in small yield, together with *p*-amino-acetophenone, by boiling aniline with acetic anhydride and zinc chloride (*Klingel*, Ber. 18, 2688).

*o*-Amino-acetophenone, b.p.  $135^\circ$  (12 mm.), is an oil, with a sweetish odour (*Camps*, Ber. 32, 3232).

*m*-Amino-acetophenone, m.p.  $99^\circ$  (*Rupe*, Ber. 34, 3522). *p*-Amino-acetophenone, m.p.  $106^\circ$ , oxime, m.p.  $147^\circ$  (*Muenchmeyer*, Ber. 20, 512).

If a pine chip is dipped into an aqueous solution of *o*-amino-acetophenone hydrochloride, it is coloured an intense orange-red. For the halochroism of aromatic aminoketones, see *Pfeiffer*, Ann. 441, 228, 265).

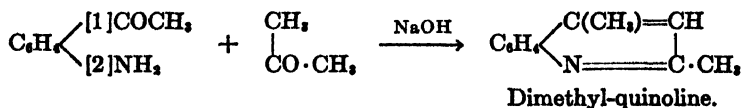
*o*-, *m*-, and *p*-Acetyl-amino-acetophenone,  $\text{CH}_3\text{CONH}\cdot\text{C}_6\text{H}_4\text{COCH}_3$ , m.p.  $77^\circ$ ,  $129^\circ$ , and  $167^\circ$ . The *p*-compound may be obtained by a rearrangement of diacetanilide, by heating with hydrochloric acid or zinc chloride (*Challaway*, Proc. 19, 50).

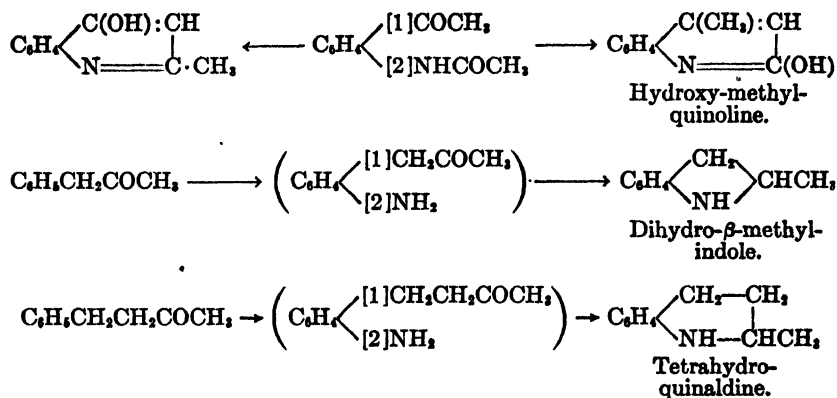
*N*-Anisal-*p*-amino-acetophenone,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{COCH}_3$ , is remarkable for the ease with which it forms liquid crystals (*Vorländer*, Z. Krist. 79, 61).

**Formation of heterocyclic compounds from aromatic *o*-aminoketones.**—1. When *o*-amino-acetophenone is digested with acetone and sodium hydroxide, *dimethyl-quinoline* is formed (*Fischer*, Ber. 19, 1037).

2. *o*-Acetyl-amino-acetophenone condenses in the presence of sodium hydroxide to  $\alpha$ -methyl- $\gamma$ -hydroxy- and  $\alpha$ -hydroxy- $\gamma$ -methyl-quinoline (*Camps*, Ber. 32, 3228).

3. When phenyl-acetone (p. 285) or benzyl-acetone is nitrated, oily nitro-compounds are formed, which give  $\beta$ -methyl-dihydro-ketol and tetrahydro-quinaldine on reduction (*Jackson*, Ber. 14, 889). The *o*-amino-compounds, possibly *o*-amino-alcohols, which are the primary products, form internal anhydrides:

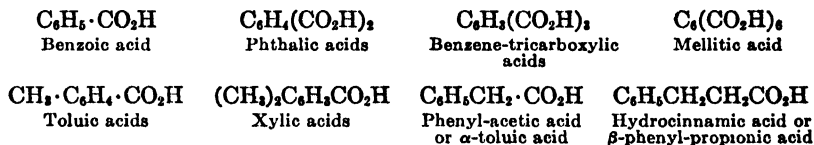




**Phenyl-ketene**,  $\text{Ph}\cdot\text{CH}:\text{CO}$ , is known only in solution. It is produced by the action of zinc filings on phenyl-chloroacetyl-chloride, and polymerises during isolation. **Phenyl-methyl-ketene**  $\text{PhCMe}:\text{CO}$ , b.p.  $74^\circ$  (12 mm.), is obtained from  $\alpha$ -phenyl- $\alpha$ -chloropropionyl chloride (*Staudinger*, *Ann.* 380, 278). **Di-phenyl-ketene**,  $\text{Ph}_2\text{C}:\text{CO}$ , see p. 554.

#### 4. Aromatic Monocarboxylic Acids

The aromatic carboxylic acids are derived from benzene and its homologues by introducing a carboxyl group in place of a hydrogen atom. This group may be directly linked to the nucleus, as in the benzene-carboxylic acids, or it may replace the hydrogen of an alkyl group in a side-chain:



It is only the monocarboxylic acids that will be discussed here.

*General methods of formation.*—1. Although the aliphatic monocarboxylic acids cannot be obtained by direct oxidation of the paraffins, the aromatic acids can be readily obtained from homologues of benzene by oxidising the side-chain to carboxyl. The importance of this reaction in establishing the constitution of compounds has already been referred to (p. 12). The most suitable oxidising agents are chromic acid, dilute nitric acid, potassium permanganate, and potassium ferricyanide.

(a) *Oxidation with chromic acid.* Only the para- and meta-derivatives of aromatic hydrocarbons, with two side-chains, are oxidised to acids by chromic acid. The para-compounds are more readily attacked than the meta-, and the ortho-compounds are either unattacked, or completely destroyed. In substituted alkyl-benzenes, the alkyl-group may be protected against oxidation by chromic acid by a negative group in the *o*-position to the alkyl group (*Wroblewski*, *Ber.* 15, 1021). Oxidation is carried out with chromic acid in glacial acetic acid, or with a mixture of potassium dichromate (3 parts), and 30-50% dilute sulphuric acid (3 parts).



(b) *Oxidation with nitric acid.* To prevent nitration, nitric acid diluted with 3 parts of water is used, and the mixture is boiled for some time. *Konowaloff* states that phenyl-nitro-paraffins are first formed, and that these are further oxidised to carboxylic acids. To remove the nitro-acids, which are invariably formed, the crude product is digested with tin and concentrated hydrochloric acid. This treatment converts the nitro-acids into amino-acids, which dissolve in hydrochloric acid.

Where a derivative has two different alkyl groups, the higher is usually attacked first by both nitric and chromic acid. Ketones are sometimes formed as intermediate products (see cymene, p. 47).

(c) Potassium permanganate and calcium permanganate (*Ullmann*, Ber. 36, 1797) will often bring about the oxidation at ordinary temperatures. In this case, ortho-di-derivatives may sometimes be oxidised without complete destruction of the benzene nucleus.

(d) Potassium ferricyanide oxidises the methyl group to carboxyl if there is a nitro-group in the ortho-position to the methyl. The oxidation does not take place if the nitro-group is in the meta-position (*Noyes*, Am. Ch. J. 11, 161).

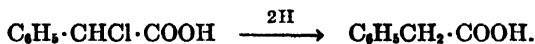
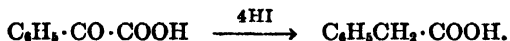
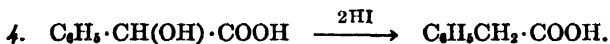
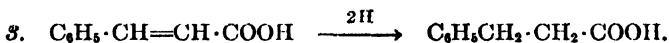
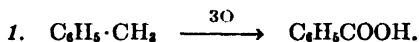
2. Oxidation of the corresponding aromatic alcohols and aldehydes.

3. By the addition of hydrogen to unsaturated monocarboxylic acids. Thus, cinnamic acid is converted into hydrocinnamic acid.

4. By reduction of phenylated hydroxy-fatty acids, phenylated halogen-substituted fatty acids, and phenylated ketonic acids.

5. Acids and amides with the same number of carbon atoms are obtained by heating the phenyl-alkyl ketones with ammonium sulphide.

The above reactions may be summarised as follows:



### Nuclear syntheses

6a. By the action of carbon dioxide on aryl magnesium halides. Thus, phenyl-magnesium iodide gives benzoic acid, and benzyl-magnesium chloride, phenyl-acetic acid. 6b. By the action of sodium and carbon dioxide on monobromobenzenes (*Kekulé*) or of carbon dioxide on aromatic hydrocarbons in the presence of aluminium chloride under high pressures and at high temperatures (Br. Pat. 307,123).

7a. By the action of sodium and ethyl chlorocarbonate on bromobenzenes (*Würtz*). 7b. By the action of carbon monoxide and steam on chlorobenzene, in the presence of catalysts, under pressure at 300° (*Maracek*, Chem. Obzor. 7, 171).

8. By fusion of salts of the sulphonic acids with sodium formate or alkali cyanide.

9. By the action of carbonyl chloride on benzene in the presence of aluminium chloride. This reaction gives rise to acid chlorides.

10a. Urea chlorides in the presence of aluminium chloride act on the benzenes in a similar way to carbonyl chloride. Amides are the first products. The urea chlorides can be replaced by (10b) cyanuric acid, or by nascent cyanic acid and hydrogen chloride. 10c. With phenylisocyanate, anilides are obtained. 10d. With phenyl-mustard oil thioanilides are formed (*Gattermann*, Ber. 32, 1116; J. pr. 59, 572).

11. By the action of benzene and aluminium chloride on aliphatic lactones or unsaturated carboxylic acids containing a double bond (*Eijkman*, Weekbl. 5, 655).

12. Through the nitriles. These may be synthesised as follows: (a) by fusing the sulphonates with potassium cyanide. (b) by the action of potassium cyanide on phenyl-alkyl chlorides. (c) by heating bromo-nitro-benzene with potassium cyanide; (d) by the action of potassium cyanide and copper sulphate on diazonium salts; (e) by heating the isonitriles. The nitriles are converted into carboxylic acids by boiling with mineral acids, or alkalis.

*Nuclear syntheses:*

6.  $\text{C}_6\text{H}_5\text{MgI} + \text{CO}_2 \longrightarrow \text{C}_6\text{H}_5\text{COOMgI}$ .
- 7a.  $\text{C}_6\text{H}_5\text{MgBr} + \text{C}_2\text{H}_5\text{OCCl} + 2\text{Na} \xrightarrow{\text{NaBr}} \text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 + \text{NaCl} + \text{NaBr}$ .
- 7b.  $\text{C}_6\text{H}_5\text{Cl} + \text{CO} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_5\text{COOH} + \text{HCl}$ .
8.  $\text{C}_6\text{H}_5\text{SO}_3\text{Na} + \text{HCOONa} \longrightarrow \text{C}_6\text{H}_5\text{COONa} + \text{NaHSO}_4$ .
9.  $\text{C}_6\text{H}_6 + \text{COCl}_2 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{COCl} + \text{HCl}$ .
- 10a.  $\text{C}_6\text{H}_6 + \text{Cl} \cdot \text{CONH}_2 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CONH}_2 + \text{HCl}$ .
- 10b.  $\text{C}_6\text{H}_6 + \text{CO} : \text{NH} \xrightarrow{\text{HCl}} \text{C}_6\text{H}_5\text{CONH}_2$ .
- 10c.  $\text{C}_6\text{H}_6 + \text{CO} : \text{NC}_6\text{H}_5 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CONHC}_6\text{H}_5$ .
- 10d.  $\text{C}_6\text{H}_6 + \text{CS} : \text{NC}_6\text{H}_5 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CSNHC}_6\text{H}_5$ .
11.  $\text{C}_6\text{H}_6 + \text{CH}_3\text{CH} : \text{CH} \cdot \text{COOH} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5(\text{CH}_2)\text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$ .
- 12a.  $\text{C}_6\text{H}_5\text{SO}_3\text{K} + \text{KCN} \longrightarrow \text{C}_6\text{H}_5\text{CN} + \text{K}_2\text{SO}_4$ .
- 12b.  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{KCN} \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CN} + \text{KCl}$ .
- 12c.  $\text{C}_6\text{H}_5\text{BrNO}_2 + \text{KCN} \longrightarrow \text{C}_6\text{H}_5(\text{NO}_2)\text{CN} + \text{KBr}$ .
- 12d.  $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{KCN} \longrightarrow \text{C}_6\text{H}_5\text{CN} + \text{N}_2 + \text{KCl}$ .
- 12e.  $\text{C}_6\text{H}_5\text{NC} \longrightarrow \text{C}_6\text{H}_5\text{CN}$ .

13. Phenyl-pyruvic acids (p. 428) (readily obtainable by nuclear syntheses, since they are the condensation products of aldehydes and hippuric acid) are oxidised to monocarboxylic acids by hydrogen peroxide (*Mauthner*, Ann. 370, 368).

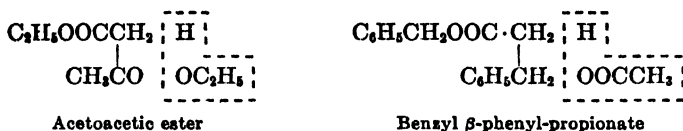


14. By the action of phenyl-alkyl chlorides, such as benzyl chloride, on sodium-acetoacetic ester, and decomposition of the ketonic esters obtained (*e.g.*, benzyl-acetoacetic ester) by alkalis.

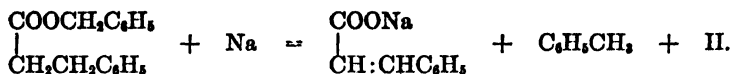
15. By the thermal decomposition of phenyl-substituted malonic acids, *e.g.*, benzyl-malonic acid.

16. Esters of aromatic monocarboxylic acids are produced when the vapours of dicarboxylic acids, or their anhydrides are passed with the vapours of alcohols, over suitable catalysts at high temperatures (Ger. Pat. 506,437).

17. By the action of sodium on the acetates, propionates, *etc.*, of the phenyl-carbinols. Thus, benzyl acetate gives benzyl phenyl-propionate, and benzyl propionate gives benzyl  $\beta$ -phenyl-butyrate. This reaction recalls the synthesis of acetoacetic ester. (Vol. I, p. 466.) In this synthesis alcohol was split off under the influence of sodium, whereas in the present reaction, acetic acid is set free:



In addition to the above, unsaturated acids are formed by secondary reactions, phenyl-acrylic acid (cinnamic acid), and phenyl-crotonic acid being formed, for example (Conrad, Ann. 193, 321; 204, 200):



*Occurrence, properties, and reactions.*—The aromatic acids occur in nature to some extent in the free state, and also as compounds in many resins and balsams, and essential oils. They are also found in the animal organism (see benzoic acid). They are also formed in the decay of proteins (see hydrocinnamic acid) (Salkowski, Ber. 16, 2313).

The aromatic acids are crystalline solids, which usually sublime without decomposition. Most of them are difficultly soluble in cold water, and are therefore precipitated from solutions of their salts by the addition of mineral acids. Electrolytic reduction (Ger. Pat. 123,554; Mettler, Ber. 39, 2933; 41, 4148), sodium amalgam, or zinc dust, will reduce some to aldehydes or alcohols, while heating with concentrated hydriodic acid, or phosphonium iodide, will convert them into hydrocarbons. Their salts are converted into salts of hexahydro-acids on hydrogenation (Ipatiev, Ber. 59, 306, 2028). When heated with lime, or better with soda-lime, they lose their carboxyl groups, and hydrocarbons are formed (*cf.* methane, Vol. I, p. 92). When polycarboxylic acids are heated with lime, acids with fewer carboxyl groups are formed as intermediate compounds. Thus, phthalic acid gives first benzoic acid, and then benzene.

The hydrogen atoms in the benzene nucleus of the acids can be substituted by the  $\text{NO}_2$ ,  $\text{SO}_3\text{H}$ ,  $\text{NH}_2$ ,  $\text{OH}$ , *etc.*, groups, in a similar way to those of the hydrocarbons and phenols. In other respects they resemble closely the fatty acids, and give rise to corresponding derivatives by replacement in the carboxyl group.

**Benzoic acid**,  $\text{C}_6\text{H}_5\cdot\text{COOH}$ , m.p.  $120^\circ$ , b.p.  $250^\circ$ , occurs in the free state in some resins, especially in gum benzoin (from *Styrax benzoin*), and in dragon's blood (from *Daemonorops Draco*). It occurs as its benzyl ester in balsam of Peru, and balsam of tolu. It is found as hippuric acid (a compound of benzoic acid and glycocoll) in the urine of herbivorous animals.

It is produced by general methods 1 and 2 from toluene (Ullmann, Ber. 36, 1798), benzyl alcohol, and benzaldehyde by oxidation, and from all hydrocarbons, alcohols, aldehydes, ketones and their deriva-

tives, which are derived from benzene by the replacement of one hydrogen atom by a univalent side-chain. Benzoic acid can also be prepared by the oxidation of pure benzene; diphenyl is probably formed first (*Kekulé*, Ann. 221, 234). Toluene can also be converted into benzyl chloride, and this can then be oxidised to benzoic acid; or benzotrichloride can be heated with water, concentrated sulphuric acid, or anhydrous oxalic acid, giving benzoic acid. It can also be obtained by the nuclear syntheses 6, 7, 8, 9, 10, and 12 from benzene, bromobenzene, sodium benzene sulphonate, and from aniline through phenyl diazonium chloride or phenyl-carbylamine. Finally it may be obtained by the addition of carbon dioxide to benzene in the presence of aluminium chloride.

*History.*—Benzoic acid was obtained by sublimation of gum benzoin at the beginning of the seventeenth century. In 1775, *Scheele* extracted the acid from the gum by means of lime water, the acid being precipitated from the solution of its calcium salt by the addition of an acid. In 1832, *Liebig* and *Wöhler*, in the course of their classical work on the benzoyl radical, determined the elementary composition of the acid, and showed its connection with benzaldehyde. They also obtained the simpler derivatives of the acid. This investigation produced such a profound impression on *Berzelius* that he suggested that the name of the new radical which contained more than two elements, and which had been called benzoyl by *Liebig* and *Wöhler*, should be *proion*, or *orthrin*, from the Greek words *πρωι*, meaning the beginning of day, or *ορθρος* meaning dawn, because he considered that the discovery meant the dawning of a new day for organic chemistry. In 1834, *Mitscherlich* distilled benzoic acid with lime and obtained benzene, and this led him to regard the acid as a derivative of this hydrocarbon. From that time, and especially since the establishment of the benzene theory by *Kekulé*, benzoic acid has been very largely used as the starting substance for the preparation of a very large number of products. It is the carboxylic acid which has been most exhaustively investigated. The study of its derivatives has been greatly facilitated by the fact that, like the acid itself, they crystallise readily.

*Preparation.*—One method of obtaining the acid is to sublime gum benzoin, or boil the resin with milk of lime, and precipitate the benzoic acid from the calcium benzoate formed by the addition of hydrochloric acid. It may also be obtained by boiling hippuric acid with hydrochloric acid. It is formed when benzyl chloride is boiled with dilute nitric acid (*Gabriel*, Ber. 10, 1275), and when phthalic anhydride is treated with superheated steam in the presence of catalysts capable of removing a carboxyl group, such as chromium, tungsten, or aluminium compounds (Fr. Pat. 692,521). When calcium phthalate is heated with calcium hydroxide to 350°, benzoic acid is formed. The hydrolysis of sulphobenzoic acids (Ger. Pat. 101,682), and the oxidation of toluene with chromic acid mixture (*Magidson*, Zhurnal. 5, 1102) also give benzoic acid. Toluene vapour may also be oxidised by atmospheric oxygen with tin vanadate as a catalyst (*Huilema*, J. Phys. Ch. 40, 531).

*Properties and reactions.*—Benzoic acid crystallises from hot water, in which it is very soluble, in white, lustrous flakes. It sublimes readily, and is volatile in steam. It is difficultly soluble in cold water (1 part in 600 of water at 0°). Its vapour possesses a distinctive odour, and produces coughing and sneezing. The benzoic acid of pharmacy is obtained by the sublimation of Siamese gum benzoin.

When heated with lime the acid gives benzene and carbon dioxide. On reduction it gives *tetra-* and *hexa-hydrobenzoic acids*.

*Salts.*—The *benzoates* are usually quite readily soluble in water. Ferric chloride gives a reddish precipitate of ferric benzoate with a neutral solution of a benzoate. The *potassium salt*,  $2C_6H_5COOK \cdot H_2O$ , crystallises in concentrically grouped

needles. The *calcium salt*,  $\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ , forms lustrous prisms or needles. The *silver salt*,  $\text{C}_6\text{H}_5\text{COOAg}$ , crystallises from hot water in lustrous flakes. It is difficultly soluble in alcohol (*Liebermann*, Ber. 35, 1094).

**Pentadeutero-benzoic acid**, m.p.  $121^\circ$ , is obtained from  $\text{C}_6\text{D}_5\text{MgBr}$  and carbon dioxide (*Erlenmeyer*, Helv. 19, 793).

**HOMOLOGUES OF BENZOIC ACID.** These compounds, like the homologues of benzaldehyde and acetophenone, can be arranged in two groups—the *alkyl-benzoic acids*, in which the carboxyl group is attached to the benzene nucleus, as in benzoic acid itself, and *phenyl-fatty acids*, in which the carboxyl group is in an aliphatic side chain of an alkyl-benzene. The members of the first class, will, of course, be more closely related to benzoic acid, than members of the second.

**ALKYL-BENZOIC ACIDS.** Toluic or methyl-benzoic acids,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , are isomeric with *phenyl-acetic acid* (p. 293). They are obtained from the three xylenes by oxidation with dilute nitric acid; from bromo- and iodo-toluenes by syntheses 6 and 1, and from the three toluidines by method 12d. *o*-Toluic acid has been prepared from phthalide by reduction with hydriodic acid (*Racine*, Ann. 239, 71), and is formed when 1,3-naphthalene derivatives, such as 1,3-dihydroxy-naphthalene, 1,3-naphthalene disulphonic acid, and 1,3-naphthol-sulphonic acid are fused with alkali, the ring being broken (*Friedländer*, Ber. 29, 1611). *p*-Toluic acid is obtained by oxidising cymene (p. 47) with dilute nitric acid.

*o*-Toluic acid, m.p.  $107^\circ$ , b.p.  $258^\circ$ .

*m*-Toluic acid, m.p.  $112^\circ$ , b.p.  $263^\circ$ .

*p*-Toluic acid, m.p.  $181^\circ$ , b.p.  $275^\circ$ .

For derivatives of toluic acids, see *van Scherpenzeel*, Rec. 20, 149.

**Ethyl-benzoic acids**,  $\text{C}_2\text{H}_5 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ . The three isomers are known. Their m.p.'s are: *o*-  $68^\circ$ , *m*-  $47^\circ$ , *p*-  $112^\circ$  (*Voszwinkel*, Ber. 21, 2830; *Aschenbrandt*, Ann. 216, 218). The *o*-acid has been obtained by reduction of acetophenone-*o*-carboxylic acid, of methyl-phthalide (*Giebe*, Ber. 29, 2533), and of phthalacetic

acid,  $\text{OCO}[1]\text{C}_6\text{H}_4[2]\text{C}:\text{CHCOOH}$ , with hydrogen iodide (*Gabriel*, Ber. 10, 2206), and of chloro-vinyl-benzoic acid with sodium amalgam (*Zincke*, Ber. 27, 2761).

**DIMETHYL-BENZOIC ACIDS**,  $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{COOH}$ . **Mesitylenic acid**, the most important of the isomerides, is formed by oxidation of mesitylene (*sym*- or 1,3,5-trimethylbenzene) with dilute nitric acid, and when heated with lime is converted into *iso*- or *m*-xylene. It was by these reactions that it was demonstrated that *m*-xylene and its oxidation products, *m*-toluic and isophthalic acids, are *m*-di-substitution products of benzene. When further oxidised mesitylenic acid gives *uvitic* and *trimesic acids*.

1,2-Dimethyl-3-benzoic acid, <sup>a</sup> *hemellitic acid*, m.p.  $144^\circ$ .

1,2-Dimethyl-4-benzoic acid, <sup>b</sup> *p-xylic acid*, m.p.  $166^\circ$ .

1,3-Dimethyl-2-benzoic acid, <sup>c</sup> m.p.  $116^\circ$ .

1,3-Dimethyl-4-benzoic acid, <sup>d</sup> *m-xylic acid*, m.p.  $127^\circ$ .

1,3-Dimethyl-5-benzoic acid, <sup>e</sup> *mesitylenic acid*, m.p.  $170^\circ$ .

1,4-Dimethyl-2-benzoic acid; <sup>f</sup> *iso-xylic acid*, m.p.  $132^\circ$ , b.p.  $268^\circ$ .

**PROPYL-BENZOIC ACIDS**,  $\text{C}_3\text{H}_7 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , *o*-, and *p*-*n*-propyl- and *o*- and *p*-*iso*-propyl-benzoic acids are known. The *p*-*iso*-

<sup>a</sup> *Jacobsen*, Ber. 19, 2518. <sup>b</sup> *Lellmann*, Ber. 24, 2115. <sup>c</sup> *Noyes*, Am. Chem. J. 20, 813. <sup>d</sup> *Bösesen*, Rec. 26, 287. <sup>e</sup> *Ciamician*, Ber. 46, 418. <sup>f</sup> *Gattermann*, Ann. 244, 54.

propyl acid, *cuminic acid*, the oxidation product of cuminal (p. 270) (*Meyer*, Ber. 11, 1790), is the most important of them. It is produced in the animal organism by oxidation of cymene (p. 47). Chromic acid oxidises it to terephthalic acid, and potassium permanganate converts it into *p*-hydroxy-isopropyl-benzoic and *p*-acetyl-benzoic acids.

*o*-*n*-Propyl-benzoic acid, m.p. 58° (*Gabriel*, Ber. 11, 1014).

*p*-*n*-Propyl-benzoic acid, m.p. 140° (*Körner*, Ann. 216, 228).

*o*-*iso*-Propyl-benzoic acid, m.p. 51° (*Kothe*, Ann. 248, 63).

*Cuminic acid*, *p*-*iso*-propyl-benzoic acid, m.p. 117° (*Meyer*, Ann. 219, 279; *Gattermann*, Ber. 20, 860).

**TRIMETHYL-BENZOIC ACIDS.** Five of these are known. Durylic acid is obtained from durenene and  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isodurylic acids from isodurene (*Janasch*, Ber. 27, 3446), by oxidation with dilute nitric acid.  $\beta$ -Isodurylic acid, or mesitylene-carboxylic acid, can also be obtained from acetyl-mesitylene (p. 284) (*Feith*, Ber. 25, 503), or from mesitylene magnesium halides with carbon dioxide (*Bamford*, J. 97, 1904).

1,2,3-Trimethyl-4-benzoic acid, m.p. 167°.\*

1,2,3-Trimethyl-5-benzoic acid,  $\alpha$ -isodurylic acid, m.p. 215°.

1,2,4-Trimethyl-5-benzoic acid, durylic acid, m.p. 151°.

1,2,4-Trimethyl-6-benzoic acid,  $\gamma$ -isodurylic acid, m.p. 127°.

1,3,5-Mesitylene-carboxylic acid,  $\beta$ -isodurylic acid, m.p. 152°.

**TETRAMETHYL-BENZOIC ACIDS.** Several of these are known: 1,2,3,4-tetramethyl-5-benzoic acid, m.p. 165°, is the oxidation product of pentamethyl-benzene (*Gottschalk*, Ber. 20, 3287); 1,2,3,5-tetramethyl-6-benzoic acid, durenene-carboxylic acid, m.p. 165° (*Gattermann*, Ber. 32, 1118); 2,3,5,6-tetramethyl-1-benzoic acid, m.p. 179° (*Jacobsen*, Ber. 22, 1221).

Pentamethyl-benzoic acid,  $(\text{CH}_3)_5\text{C}_6\text{COOH}$ , m.p. 210°, is made by methods 6 and 9, above (*Jacobsen*, Ber. 22, 1221; *Grignard*, C.r. 198, 625).

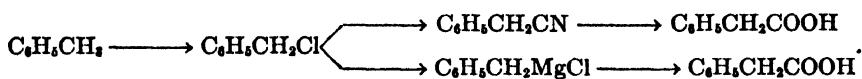
**PHENYL-FATTY ACIDS.** The most important representatives of this class are phenyl-acetic acid, or  $\alpha$ -toluic acid,  $\beta$ -phenyl-propionic acid, or hydrocinnamic acid, and  $\alpha$ -phenyl-propionic acid, or hydratropic acid. The syntheses of the phenyl-fatty acids are exactly the same as those of the fatty acids themselves (Vol. I, p. 297), and they undergo similar reactions. The general methods of formation numbers 2, 3, 4, 5, 6, 11, 12b, 13, 14, 15, and 17 (p. 288) are those usually employed for their preparation. Aryl-acetic acids may also be obtained from aromatic aldehydes by the action of mandelic nitriles (*Ar. Pharm.*, 271, 432).

*p*-Bornyl-benzoic acid,  $\text{C}_{10}\text{H}_{17}\text{C}_6\text{H}_4\text{COOH}$ , m.p. 195°, is obtained from bornyl-benzene by converting it into its *p*-bromo-derivative, acting on this with magnesium, and decomposing the Grignard compound formed with carbon dioxide (*Karienski*, Roc. 15, 92).

**Phenyl-acetic acid**,  $\alpha$ -toluic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ , m.p. 76°, b.p. 265.5°, occurs in Japanese peppermint oil as a  $\beta$ , $\gamma$ -hexenol ester (*Walbaum*, J. pr. 96, 245). The acid is obtained from toluene in the same way as acetic acid is obtained from methane. Toluene is first converted into benzyl chloride, and this into benzyl cyanide, which is

\* The name "prehnitic acid," formerly given to this substance, has been discarded as the alcohol, "prehnilol," has been found not to be a single substance. There also appears to be some doubt about the uniformity of isodurene.

then digested with sulphuric acid (*Staedel*, Ber. 19, 1950; *Wislicenus*, Ber. 20, 592). Another method is to convert benzyl chloride, in ether solution, into benzyl-magnesium chloride by the action of magnesium, and to decompose this with carbon dioxide (*Houben*, Ber. 35, 2523; *Zelinsky*, Ber. 35, 2694):



It can also be obtained by reduction of phenyl-chloroacetic acid,  $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{COOH}$  (*Spiegel*, Ber. 14, 240), phenyl-glycolic or mandelic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{COOH}$ , and phenyl-glyoxylic acid,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{COOH}$ .

It is produced when phenyl-malonic acid is heated (see method 15), and is one of the products of decay of proteins (*Salkowski*, Ber. 12, 649). It may also be prepared from bromobenzene, chloroacetic ester, and copper (*Zincke*, Ber. 2, 738); by heating acetophenone with yellow ammonium sulphide (cf. method 5, p. 288), and by oxidising phenyl-pyruvic acid with hydrogen peroxide. It is oxidised by chromic acid to benzoic acid. Chlorine, on heating, converts it into phenyl-chloroacetic acid, while in the cold the halogens replace nuclear hydrogen atoms.

Its esters can be alkylated in the methylene group by means of alkyl halides and sodamide (*Ramart*, C.r. 178, 1583). For their reactions with alkyl-magnesium halides, see *Ivanov*, Bull. 49, 377. With metallic potassium, phenylacetic acid forms an enol compound,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{OR})(\text{OK})$ , which reacts further both with more ethyl phenylacetate and with reactive halides, C- and O-substituted derivatives being formed (*Scheibler*, Ber. 60, 558, 564; 63, 1562). Esters of phenyl-orthoacetic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{OR})_2$ , have been obtained from the reaction products of phenyl-acetonitrile, primary alcohols, and hydrogen chloride (*Sah*, J. 1931, 305).

**TOLYL-ACETIC ACIDS**,  $\alpha$ -xylic acids,  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{COOH}$ . The three isomeric acids have been obtained from the three xylyl bromides. Their melting points are: *o*- 89°, *m*- 61°, *p*- 91° (*Claus*, Ber. 20, 2051; *Ruhemann*, Ber. 24, 3965).  $\alpha$ -Dialkyl-toluic acids have been prepared from toluene and  $\alpha$ -bromo-isobutyric and  $\alpha$ -bromo-methyl-ethyl-acetic esters by the action of aluminium chloride (*Rupe*, Ber. 44, 1218). *p*-Xylyl-acetic acid,  $(\text{CH}_3)_2[1,4]\text{C}_6\text{H}_3\cdot\text{CH}_2\text{COOH}$ , m.p. 128°, is obtained by the action of ammonium sulphide on acetop-xylene (*Guerbet*, C.r. 125, 34).

**Hydrocinnamic acid**,  $\beta$ -phenyl-propionic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COOH}$ , m.p. 47°, b.p. 280°, is isomeric with  $\alpha$ -phenyl-propionic acid, the three ethyl-benzoic acids, and the six dimethyl-benzoic acids. It is obtained by reduction of cinnamic acid,  $\text{C}_6\text{H}_5\text{CH}:\text{CHCOOH}$ , either electrolytically, using a mercury cathode (*Rupe*, Helv. 14, 49), by the action of sodium amalgam, or hydrogen iodide (Ber. 30, 1680). It can also be obtained by the action of carbon dioxide on phenyl-ethyl-magnesium bromide,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{MgBr}$  (*Grignard*, C.r. 138, 1048); by the action of yellow ammonium sulphide on propiophenone; from phenyl-ethyl cyanide (*Fittig*, Ann. 156, 249); from benzyl-acetoacetic ester (*Merz*, Ber. 10, 758); from benzyl-malonic ester (*Conrad*, Ann. 204, 176); in the form of its benzyl ester by the action of sodium on benzyl acetate (*Conrad*, Ann. 193, 300); and by decay of proteins (*Salkowski*, Ber. 12, 649). Cf. methods of formation 5, 6, 14, 15, and 17, p. 288). Chromic acid oxidises it to benzoic acid.

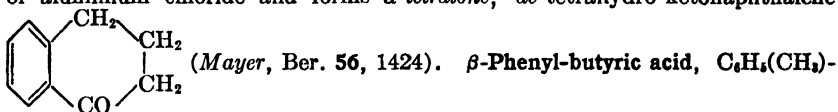
Halogeno-hydrocinnamic acids with halogen in the side chain are readily obtained from cinnamic acid by the addition of hydrogen halides or halogens.

They will be described after phenyl-lactic and phenyl-glyceric acids. Homologous  $\beta$ -aryl-propionic acids are obtained from aromatic carboxylic acids by converting them into substituted benzoyl-acetic esters and hydrogenating these catalytically (Ar. Pharm., 271, 437).

**Hydratropic acid,  $\alpha$ -phenyl-propionic acid**,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\cdot\text{COOH}$ , b.p.  $265^\circ$ , is an oil, volatile in steam. It is produced by reduction of atropic acid, or  $\alpha$ -phenyl-acrylic acid,  $\text{C}_6\text{H}_5\text{C}(\text{=CH}_2)\cdot\text{COOH}$ , by the action of hydriodic acid on the addition product of hydrogen cyanide and acetophenone (the nitrile of atrolactic acid) (Janssen, Ann. 250, 135), or by hydrolysis of its nitrile,  $\text{C}_6\text{H}_5\text{CHCH}_3\text{CN}$ . Attempts to resolve this acid into its optical isomers are described by Raper (J. 123, 2557).

*Higher homologues* of these acids have been obtained mainly by the following methods: (1) reduction of homologues of cinnamic acid (p. 469), which are readily prepared by Perkin's syntheses from the aromatic aldehydes; (2) reduction of homologues of mandelic acid, obtained from homologues of phenyl-glyoxylic acid. The latter are obtained by oxidising homologues of acetyl-benzene with potassium permanganate; (3) by the action of yellow ammonium sulphide on the alkyl-phenyl ketones; (4) from alkyl-benzyl cyanides, produced by the action of alkyl halides on sodio-benzyl cyanide; (5) by the action of benzene and aluminium chloride on aliphatic lactones and olefine-carboxylic acids.

**$p$ -Methyl-hydratropic acid,  $\alpha$ - $p$ -tolyl-propionic acid**,  $p\text{-C}_7\text{H}_7\text{CH}(\text{CH}_3)\text{COOH}$ , m.p.  $34^\circ$ , is obtained from  $p$ -xylyl cyanide by method 12b (Rupe, Helv. 7, 654).  **$\gamma$ -Phenyl-butyric acid**,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ , m.p.  $51.7^\circ$ , is obtained by the reduction of phenyl-butyrolactone or phenyl-crotonic acid (Kipping, J. 75, 140) from  $\omega$ -bromo-propyl-benzene with magnesium and carbon dioxide (Rupe, Ber. 43, 1233); by the action of ammonium sulphide on phenyl-propyl ketone (Willgerodt, J. pr. 80, 198); and from  $\beta$ -benzoyl-propionic acid by Clemmensen's method (Overbough, Org. Synth. 15, 64). Its chloride condenses under the action of aluminium chloride and forms  $\alpha$ -tetralone, ac-tetrahydro-ketonaphthalene



**$\beta$ - $p$ -Tolyl-butyric acid, curcumaic acid**,  $p\text{-C}_7\text{H}_7\text{CH}(\text{CH}_3)\text{CH}_2\cdot\text{COOH}$ , m.p.  $33\text{--}34^\circ$ , is obtained by the action of sodium hypobromite on curcumone (p. 285), or synthetically from methyl- $p$ -tolyl ketone by Reformatsky's reaction (Helv. 7, 654).  **$\alpha$ -Phenyl-isobutyric acid**,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{COOH}$ , m.p.  $78^\circ$ , b.p.  $150\text{--}155^\circ$  (10 mm.), is obtained from benzene, aluminium bromide, and  $\alpha$ -bromo-isobutyric acid (Wallach, C. 1899, II, 1047).  **$\beta$ -Phenyl-isobutyric acid**,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{COOH}$ , m.p.  $37^\circ$ , b.p.  $272^\circ$ , can be resolved into optical isomerides by its quinine salt (Kipping, Proc. 18, 33).  **$\delta$ -Phenyl-valeric acid**,  $\text{C}_6\text{H}_5(\text{CH}_2)_4\text{COOH}$ , m.p.  $59^\circ$ , is obtained by the reduction of phenyl-coumalin with hydriodic acid (Leben, Ber. 29, 1675; Severini, Gazz. 26, II, 326).

**Phenyl-tert.-butylacetic acid**,  $(\text{CH}_3)_3\text{C}\cdot\text{CHC}_6\text{H}_5\cdot\text{COOH}$ , m.p.  $105^\circ$ , is obtained from the tert.-butyl ketone via the carbinol, by acting on its bromide with magnesium, followed by carbon dioxide (Ford, Am. 57, 2619).  **$\alpha$ -Phenyl-isovaleric acid**,  $(\text{CH}_3)_2\text{CH}\cdot\text{CHC}_6\text{H}_5\cdot\text{COOH}$ , m.p.  $59^\circ$ , and  **$\alpha$ -methyl- $\beta$ -phenyl-butyric acid**,  $\text{CH}_3\text{CHC}_6\text{H}_5\cdot\text{CHCH}_2\cdot\text{COOH}$ , m.p.  $132^\circ$ , are obtained from isopropylidene-acetic and tiglic acid with benzene and aluminium chloride (Eijkman, Weekbl. 5, 655).  **$\beta$ -Phenyl-isovaleric acid**,  $[\text{C}_6\text{H}_5(\text{CH}_2)_2]\text{C}\cdot\text{CH}_2\text{COOH}$ , m.p.  $58^\circ$ , is obtained from methyl- $\beta$ -phenyl-isobutyl ketone by the action of sodium hypobromite, or from  $\alpha$ -chloro-isopropyl-benzene with sodio-malonic



ester (*Hoffman*, J. 51, 2542).  $\alpha$ -Methyl- $\gamma$ -phenyl-butyric acid,  $C_6H_5CH_2CH_2CH(CH_3)COOH$ , m.p.  $67^\circ$ , has been prepared from phenyl-isobutyl ketone and ammonium sulphide (*Willgerodt*, J. pr. 80, 198). 15-Phenyl-pentadecanic acid, m.p.  $60^\circ$ , and 22-phenyl-behenic acid, m.p.  $81^\circ$ , have been prepared from the corresponding 13-keto-acids by Clemmensen's method (*Hill*, J. 1936, 281).

### Functional Derivatives of Aromatic Monocarboxylic Acids

The derivatives of benzoic acid and its homologues may be arranged in two groups. The first comprises those compounds resulting from reaction with the carboxyl group (see acetic acid, Vol. I, p. 300), and the second, the aromatic substitution products, with the exception of the phenol-monocarboxylic acids. The first group may be further subdivided into (A) the benzoyl compounds, (B) the benzenyl compounds, containing the group  $PhC\equiv$ , and derivatives of orthobenzoic acid,  $C_6H_5C(OH)_3$ . Of all the carboxylic acids the chemistry of benzoic acid has been the most fully investigated.

#### A. BENZOYL COMPOUNDS

**1. ESTERS OF THE MONOBASIC AROMATIC ACIDS.** The benzoic esters of alcohols and phenols are prepared in the same way as the acetic esters. Like the latter, they are frequently used for the determination of the number of hydroxyl groups in a compound. They are formed (1) by the action of hydrogen chloride on an alcoholic solution of benzoic acid. In the substituted benzoic acids it is found that the *o*-substituted acids take a longer time to esterify than the *m*- and *p*-acids (*Kellas*, Z. physik. Ch. 24, 221). In the di-*o*-substituted acids, such as mesitylene carboxylic acid, 2,6-dibromo-, 2,4,6-tribromo-, and 2,4,6-trinitro-benzoic acids, ester formation is exceedingly slow when the acid is boiled with an alcohol and hydrogen chloride, that it may almost be said not to take place at all (*Rosanoff*, Z. physik. Ch. 66, 275). Esters are, however, readily formed by heating these acids to  $180$ – $200^\circ$  with an alcohol, even in the absence of a catalyst. The esters are also readily obtained (2) by the action of alkyl halides on the silver salts of the acids, or by the action of dimethyl sulphate on the alkali salts; (3) by treating the acids with diazomethane (*Pechmann*, Ber. 31, 501). The esters of benzoic acid are also produced (4) by the action of benzoyl chloride, or benzoic anhydride on alcohols, alcoholates, phenols, and phenolates. In carrying out reaction (4) it is often advisable to dissolve the alcohol or phenol in pyridine and to add benzoyl chloride to this solution, or to shake the alkaline, aqueous solution of the alcohol with benzoyl chloride until there is a permanent alkaline reaction (*Baumann*, Ber. 19, 3218). The benzoyl ethers of the polyhydric alcohols, or polyhydroxyaldehydes, such as the glucoses, have been obtained in this way, and nearly all have been completely benzoylated (*Skraup*, Mo. 10, 389). (5) the esters may also be prepared by passing a mixture of the vapours of the acid and alcohol over thorium oxide heated to  $400^\circ$  (*Sabatier*, C.r. 152, 358).

Methyl benzoate, m.p.  $-12^\circ$ , b.p.  $199^\circ$ . Ethyl benzoate, m.p.  $-34^\circ$ , b.p.  $213^\circ$ . *n*-Propyl benzoate, b.p.  $231^\circ$ . *n*-Butyl benzoate, b.p.  $249^\circ$ . Glycol monobenzoate, m.p.  $45^\circ$  (Ger. Pat. 298,185). Glycol dibenzoate, m.p.  $73^\circ$  (*Gabriel*, Ber. 23, 2498). Glycerol tribenzoate, m.p.  $76^\circ$  (*Balbiano*, Gazz. 152, 358). Erythritol tetrabenzoate, m.p.  $187^\circ$ . Mannitol hexabenzoate, m.p.  $124^\circ$ . Glucose pentabenzoate, m.p.  $179^\circ$ . For the catalytic reduction of benzoic esters, see *Mitsui*, Mem. Kyoto. 18, 329.

Methylene dibenzoate,  $CH_2(OCOC_6H_5)_2$ , m.p.  $96^\circ$ , is prepared by heating benzoyl chloride with trioxymethylene and zinc chloride, the compound  $Cl-CH_2OCOC_6H_5$ , being formed intermediately (*Henri*, C.r. 133, 96; *Descudé*, C.r. 133, 371).

**O-Benzoyl-glycolic acid**,  $C_6H_5CO \cdot OCH_2 \cdot COOH$ , forms large prisms. It is prepared by the action of nitrous acid on hippuric acid, and its esters are obtained from sodium benzoate and chloroacetic ester. Phenyl benzoate, m.p.  $71^\circ$ , b.p.  $314^\circ$  (*Döbner*, Ann. 210, 255; *Heiber*, Ber. 24, 3685). Benzyl benzoate, m.p.

21°, b.p. 323° (*Claisen*, Ber. 20, 647), occurs in balsam of Peru (*Kraut*, Ann. 152, 130) and in oil of carnation. For its preparation by Cannizzaro's method, see *Kamm*, Am. Pharm. 11, 599. For the benzoyl compounds of homologues of phenol, see pp. 220, 223, 227.

Methyl *o*-, *m*-, and *p*-toluates,  $\text{CH}_3\text{C}_6\text{H}_4\text{COOCH}_3$ , b.p. 213° and 221°, and m.p. 34°, respectively (*van Scherpenzeel*, Rec. 20, 149). For esters of toluic acids with aliphatic mercaptans, see *Kimball*, Read, Am. 38, 2757.

Ethyl phenylacetate,  $\text{C}_6\text{H}_5\text{CH}_2\text{COOC}_2\text{H}_5$ , b.p. 226°, is obtained by the action of alcohol and hydrogen chloride on benzyl cyanide (*Wislicenus*, Ann. 296, 361). Phenyl ester, m.p. 38°, b.p. 180° (15 mm.). Ethyl phenylacetate has a faint odour of honey. Like diethyl malonate, it adds on  $\alpha, \beta$ -unsaturated ketones and esters under the influence of sodium ethoxide (*Borsche*, Ber. 42, 4996). With ethyl nitrate and potassium ethoxide it gives phenyl-nitroacetic ester,  $\text{C}_6\text{H}_5\text{CH}(\text{NO}_2)\text{COOR}$ , which easily loses its carbethoxyl group and forms phenyl-nitromethane (p. 256). With ethyl nitrite and potassium ethoxide, phenyl-isotri-nitroso-acetic ester,  $\text{C}_6\text{H}_5\text{C}(\text{NOH})\text{CO}_2\text{R}$ , is formed (*Wislicenus*, Ber. 42, 1930). Ethyl  $\beta$ -phenyl-propionate, b.p. 248°.

**2. AROMATIC ACID HALIDES.** These compounds are prepared by similar methods to the corresponding aliphatic compounds (Vol. I, p. 314).

**Benzoyl chloride**,  $\text{C}_6\text{H}_5\text{COCl}$ , m.p.  $-0.5^\circ$ , b.p. 198°, is isomeric with chlorobenzaldehydes,  $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ . It is a liquid with a pungent smell. It is obtained by the action of phosphorus pentachloride, phosphorus trichloride, thionyl chloride, or phosphorus pentoxide and hydrogen chloride, on benzoic acid; by the action of chlorine on benzaldehyde, and by the action of phosphorus oxychloride on sodium benzoate. The chlorides of benzene-carboxylic acids are obtained by the action of carbonyl chloride, or oxalyl chloride, on the hydrocarbons in the presence of aluminium chloride (*Staudinger*, Ber. 41, 3566), and by the action of anhydrous oxalic acid, or water in the presence of a catalyst, on benzotrichloride (*Anschütz*, Ann. 226, 20; Ger. Pat. 331,696).

Benzoic acid combines with antimony pentachloride to give the compound  $\text{PhCOOH}\cdot\text{SbCl}_5$ , m.p. 71°. When this is heated, benzoyl chloride is formed (*Rosenheim*, Ber. 35, 1117).

Benzoyl chloride was the first acid chloride of a carboxylic acid to be discovered, and its history has already been given in connection with the aliphatic acid chlorides. It is a readily accessible and very reactive substance, and few carbon compounds have had a more varied application in preparative organic chemistry.

The acid chlorides react with diazomethane to give aryl- $\omega$ -chloromethyl ketones,  $\text{ArCO}\cdot\text{CH}_2\text{Cl}$  (*Clibbens*, J. 107, 1491), but benzoyl chloride in ether solution gives only a little chloro-acetophenone, the chief product being *diazo-acetophenone*,  $\text{C}_6\text{H}_5\text{COCHN}_2$  (*Bradley*, *Robinson*, Nature, 122, 130). Catalytic reduction of the acid chlorides gives rise to the alcohol, aldehyde, ester, or hydrocarbon, according to the conditions (*Rosenmund*, Ber. 54, 638). For molecular compounds of benzoyl chloride with aluminium chloride and bromide see *Menschutkin*, C. 1911, I, 481.

Toluy chlorides, *o*-, *m*-, and *p*-, b.p. 212°, 220°, and 95° (10 mm.), respectively. Phenyl-acetyl chloride,  $\text{C}_6\text{H}_5\text{CH}_2\text{COCl}$ , b.p. 102° b.p. 102° (17 mm.) (*Anschütz*, Ber. 20, 1389).

Benzoyl bromide,  $\text{C}_6\text{H}_5\text{COBr}$ , m.p. 0°, b.p. 218°, is obtained by the action of phosphorus tribromide on benzoic acid (*Claisen*, Ber. 14, 2473). Benzoyl iodide, m.p. 3°, b.p. 117° (14 mm.), is obtained from benzoyl chloride and potassium iodide or magnesium iodide (*Kishner*, C. 1909, II, 1132). Benzoyl fluoride,

b.p. 155°, is obtained by the action of zinc fluoride, or better, sodium fluoride, on benzoyl chloride at 150° (*Dann*, J. 1933, 15), or by the action of potassium hydrogen fluoride (*Tseng*, J. Chin. 4, 22).

*Benzoyl azimide or nitride*, which resembles the benzoyl halides in its properties, will be dealt with below, in connection with benzoyl-hydrazine.

*Mixed anhydrides of aromatic and inorganic acids* are analogous to the acid halides.

**Benzoyl nitrate**,  $C_6H_5COONO_2$ , is a bright yellow, unstable oil, formed by the action of silver nitrate on benzoyl chloride at low temperatures. When heated it decomposes into benzoic anhydride and oxides of nitrogen. It is decomposed by water into benzoic and nitric acids. It behaves as a nitrating reagent towards aromatic substances (*Francis*, Ber. 39, 3798). **Benzoyl nitrite**,  $C_6H_5COONO$ , is an unstable oil obtained by the action of nitrosyl chloride on silver benzoate (*Francesconi*, Gazz. 34, I, 435).

**Benzoic-boric anhydride**,  $(C_6H_5COO)_2B$ , m.p. 145°, is obtained by heating benzoic acid with acetic-boric anhydride, and *benzoic-arsenious anhydride*,  $(C_6H_5COO)_2As$ , m.p. 155°, is obtained by fusing benzoic acid with acetic-arsenious anhydride (*Pictet*, Ber. 36, 2224; Bull. [3], 33, 1139).

**3. ACID ANHYDRIDES.** **Benzoic anhydride**,  $(C_6H_5CO)_2O$ , m.p. 42°, b.p. 360°, is obtained from benzoyl chloride and sodium benzoate or silver benzoate; from benzoyl chloride and benzotrichloride on heating with anhydrous oxalic acid or oxalyl chloride (*Adams*, Am. 40, 424); from benzoyl chloride by the action of lead nitrate or sodium nitrite (*Lachowicz*, Ber. 17, 1282; *Minnumi*, Gazz. 20, 655); from benzoyl chloride by the action of potassium metabisulphite and tertiary bases (*Gazopulos*, J. 1931, 1500), or with  $\frac{1}{2}$  mol. of water in the presence of a catalyst, such as phosphorus oxychloride at 260–280° (Ger. Pat. 520,153); and by the action of concentrated sulphuric acid on benzotrichloride (Ger. Pat. 6,689; Ber. 12, 1495). Mixed anhydrides are obtained from benzoic acid by the action of acid chlorides or anhydrides in the presence of pyridine or quinoline (Ger. Pat. 117,267; *Kaufmann*, Ber. 42, 3483). **Aceto-benzoic anhydride**,  $C_6H_5COO \cdot OC \cdot CH_3$ , m.p. 10°, b.p. 125–140° (17 mm.), decomposes into acetic and benzoic anhydrides on heating. **Benzoic-carbonic anhydride**,  $(C_6H_5COO)_2CO$ , is an oil, obtained from benzoic acid, carbonyl chloride, and pyridine, and loses carbon dioxide even at ordinary temperature.

*o*- and *p*-**Toluic anhydrides**, m.p. 37° and 95°, respectively. **Phenylacetic anhydride**,  $(C_6H_5CH_2CO)_2O$ , m.p. 72° (*Anschtütz*, Ber. 20, 1391; *Bakunin*, Gazz. 46, I, 77).

**4. ACYL PEROXIDES.** **Benzoyl peroxide**, *dibenzoyl peroxide*,  $(C_6H_5CO)_2O_2$ , m.p. 104° deflagrates on heating and often explodes spontaneously even at ordinary temperature (*Namelkin*, J. Russ. 62, 2193). It is prepared by the action of sodium peroxide, barium peroxide, or hydrogen peroxide and sodium hydroxide on benzoyl chloride (*Pechmann*, Ber. 27, 1511; *Vanino*, Ber. 29, 1727; 30, 2003; 33, 1043). It reacts with carbon tetrachloride to form  $\omega$ -trichloro-*p*-toluic acid  $Cl_3C[4]C_6H_4[1]COOH$  (*Bösesken*, Rec. 43, 869). It reacts in two different ways with aromatic hydrocarbons, aliphatic alcohols and acids: (a)  $(C_6H_5CO)_2O_2 + RH = C_6H_5COOH + C_6H_5 \cdot R + CO_2$ , and (b)  $(C_6H_5CO)_2O_2 + RH = C_6H_5COOR + C_6H_5 + CO_2$ . See *Gelissen*, Ber. 58, 765, 984, for the quantitative investigation of these reactions with various groups of compounds. Benzoyl peroxide is a bleaching agent, and is marketed under the name of *Lucidol*. When benzoyl peroxide dissolved in ether, or preferably in benzene (*Wieland*, Ann. 446, 28), is treated with sodium ethoxide, ethyl benzoate and benzoyl-sodium-hydrogen peroxide are formed:



Dilute sulphuric acid, or even carbonic acid, liberate **benzoyl-hydroperoxide**, *perbenzoic acid*,  $C_6H_5COOOH$ , m.p. 42–43°, from the latter. It is a compound which resembles hydrogen peroxide closely. It has also been prepared by the action of hydrogen peroxide and sodium hydroxide, or of sodium peroxide on benzoyl chloride (*Brooks*, Am. 55, 4309), and by the action of sodium ethoxide on benzoyl peroxide (*Pummerer*, Ber. 66, 336). A mixture of benzoyl-hydroperoxide and benzaldehyde readily and completely breaks down into two mols. of benzoic

acid. Perbenzoic acid is the primary product in the autoxidation of benzaldehyde in the air (p. 269), and is formed when benzaldehyde, dissolved in acetone, is aerated in sunlight, or in powerful artificial light (Dutch Pat. 17,393). A mixture of benzaldehyde and acetic anhydride is oxidised by air to benzoyl-acetyl peroxide,  $C_6H_5COOOCOCH_3$ , m.p.  $38^\circ$ , perbenzoic acid being the primary product, it being then acetylated (Baeyer, Ber. 33, 1569; Freer, Am. J. 27, 161). Perbenzoic acid quantitatively saturates double bonds with formation of ethylene oxides (Meerwein, J. pr. 113, 9; Nametkin, J. pr. 115, 56). For the course of this reaction see Böseken, Rec. 48, 363; J. pr. 131, 285. Perbenzoic acid oxidises sulphides to sulphoxides and sulphones (Lewin, J. pr. 128, 171). For action of benzoyl-hydroperoxide on triphenylmethyl, see Medwedew, Ber. 65, 137.

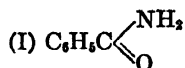
**5. THIO- AND DITHIO-ACIDS.** Thiolbenzoic acid,  $C_6H_5COSH$ , m.p.  $24^\circ$ , is formed by the action of alcoholic potassium sulphide on benzoyl chloride, or by the action of carbon oxy sulphide on phenyl-magnesium bromide, when triphenyl-carbinol is a by-product (Weigert, Ber. 36, 1010). Thiol-*p*-toluic acid,  $CH_3C_6H_4COSH$ , m.p.  $44^\circ$ . Benzoyl sulphide, thiolbenzoic-sulphanhydride,  $(C_6H_5CO)_2S$ , m.p.  $48^\circ$ , is obtained by the action of two mols. of benzoyl chloride on one of sodium sulphide. Benzoyl disulphide,  $(C_6H_5CO)_2S_2$ , m.p.  $130^\circ$ , is obtained by exposing an ether solution of thiolbenzoic acid to air (Cloez, Ann. 115, 27), or when salts of thiolbenzoic acid are oxidised with potassium ferricyanide (Fromm, Ber. 40, 2862). Benzoyl polysulphides (tri- and tetra-sulphides) are obtained by the action of sulphur chloride,  $S_2Cl_2$ , or iodine, on potassium thiolbenzoate, or by the action of hydrogen peroxide on thiolbenzoic acid (Shelton, Am. 58, 1282; Moresz, Ar. Pharm. 25, 397). For thiolbenzamides and thiolbenzanilides, see p. 308.

Dithiobenzoic acid,  $C_6H_5CSSH$ , is a heavy, mauve-coloured, unstable oil, obtained by the action of alcoholic potassium sulphide on benzotrichloride (Fleischer, Ann. 140, 240), by the action of carbon disulphide on phenyl-magnesium bromide (Houben, Ber. 39, 3219), and by the action of hydrogen persulphide and zinc chloride on benzaldehyde (Höhn, J. pr. 82, 436; Ger. Pat. 214,888). Methyl ester, b.p.  $155^\circ$  (12 mm.); ethyl ester, b.p.  $167^\circ$  (16 mm.); both are red oils. Lead salt, m.p.  $204.5^\circ$ , purple leaflets. Iodine oxidises the solutions of the alkali salts to dark red needles of thio-benzoyl-disulphide,  $(C_6H_5CS)_2S_2$ , m.p.  $117^\circ$ . 4-Carbitio-toluic acid,  $CH_3C_6H_4CSSH$ , m.p.  $27^\circ$ , is obtained from *p*-tolyl-magnesium bromide; methyl ester, b.p.  $130^\circ$  (3 mm.). Dithio-phenylacetic acid,  $C_6H_5CH_2CSSH$ , is an orange-coloured oil obtained by the action of carbon disulphide on benzyl-magnesium chloride; lead salt, m.p.  $149^\circ$ , golden-yellow needles. Phenyl-thioacetyl-disulphide,  $(C_6H_5CH_2CS)_2S_2$ , m.p.  $78^\circ$  (Houben, Ber. 39, 3227). Phenyl-*p*-tolyl-ketosulphone,  $C_6H_5CO \cdot SO_2C_6H_4CH_3$ , obtained from benzoyl chloride and sodium toluene-sulphinate, forms a hydrate, m.p.  $80^\circ$  (Ger. Pats. 100779/80).

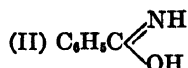
Acyl thiosulphites, such as  $(C_6H_5CO)_2O_2S_2$ , are mixed anhydrides of an aromatic carboxylic acid and a hypothetical acid of sulphur,  $Se(OH)_2$ . They are obtained by the action of metallic benzoates and metallic salts of other aromatic acids on sulphur chloride:  $2Ar \cdot COOAg + S_2Cl_2 = 2AgCl + (ArCO)_2O_2S_2$  (Denham, J. 103, 1861).

**SELENO-BENZOIC ACID**,  $C_6H_5COScH$ , rose-coloured crystals, m.p.  $133^\circ$ , has been prepared from benzoyl chloride and bromo-magnesium-seleno-hydride,  $BrMgScH$  (Mingoa, Gazz. 56, 835).

**6. ACID AMIDES.** The methods of formation and reactions of the acid amides have been considered at sufficient length in connection with the amides of aliphatic acids. Attention was drawn to the fact that the amides of the carboxylic acids could have two constitutional formulae. Thus, benzamide has two formulae:



and



The imino-ethers are derived from the second formula (see silver benzamide). In addition to the methods of formation given under

aliphatic acid amides, the amides of benzene-carboxylic acids can be obtained by the action of aluminium chloride on aromatic hydrocarbons and urea chlorides (p. 289).

**Benzamide**,  $C_6H_5 \cdot CO \cdot NH_2$ , m.p. stable form,  $128^\circ$ , unstable form,  $115^\circ$  (Müller, Z. physik. Ch. 86, 228), b.p.  $288^\circ$ , is formed: (1) by the action of gaseous ammonia, ammonium hydroxide, or ammonium carbonate on benzoyl chloride (see tribenzamide); (2) by the action of ammonia on ethyl benzoate; (3) by heating benzoic acid and ammonium thiocyanate to  $170^\circ$ ; (4) by hydrolysis of benzonitrile with the requisite amount of alcoholic potash; (5) by the action of urea chloride on benzene in the presence of aluminium chloride (Gattermann, Ann. 244, 50; Rabaut, Bull. [3], 21, 1075). It is readily soluble in hot water, alcohol, and ether.

**Sodium benzamide**,  $C_6H_5CONHNa$ , or  $C_6H_5C(:NH)ONa$ , is formed by the action of metallic sodium on benzamide in benzene solution (Curtius, Ber. 23, 3038). When heated with esters it forms mixed diacyl-imides (Wheeler, Am. J. 28, 453; Thitherley, J. 81, 1520).

**Silver benzamide**,  $C_6H_5CO \cdot NHAg$ , or  $C_6H_5 \cdot C(:NH)O \cdot Ag$ , is obtained by precipitating an aqueous solution containing benzamide and silver nitrate with the calculated quantity of sodium hydroxide. When digested with ethyl iodide it gives benzimido-ethyl ether (p. 308) (Tafel, Ber. 23, 1550). Certain benzarsinic acids such as  $H_2N \cdot CO \cdot \text{C}_6H_4 \cdot AsO_2H_2$ , derived from benzamide, are trypanocides (Gough, King, J. 1930, 669).

**Dibenzamide**,  $(C_6H_5CO)_2NH$ , m.p.  $148^\circ$ , is obtained by the action of fuming sulphuric acid on benzonitrile, or from benzoyl chloride and benzonitrile with aluminium chloride. When distilled dibenzamide breaks down into benzonitrile and benzoic acid, even at low pressures. **Sodium dibenzamide**,  $(C_6H_5CO)_2NNa$ , is a lustrous white powder. It is formed by the action of sodium on dibenzamide in xylene solution.

**Tribenzamide**,  $(C_6H_5CO)_2N$ , m.p.  $202^\circ$ , is formed by the action of benzoyl chloride in ether solution on sodium dibenzamide, and, together with benzamide and dibenzamide, when benzoyl chloride is acted upon by ammonium carbonate (Jaffe, Ber. 25, 3120). **Benzoyl-cyanamide**,  $C_6H_5CONHCN$ , m.p.  $141-142^\circ$ , is obtained by the action of cyanamide and sodium hydroxide (or commercial sodium cyanamide) on benzoyl chloride below  $5^\circ$  (Diels, Ber. 45, 874).

**Benzoyl-chloroamide**,  $C_6H_5CONHCl$ , m.p.  $113^\circ$ . **Benzoyl-bromoamide**,  $C_6H_5CONHBr$ , m.p.  $170^\circ$  (decomp.). **Dibenzamide chloride**,  $(C_6H_5CO)_2NCl$ , m.p.  $89^\circ$  (Chattaway, Proc. 18, 165). **Methyl- and dimethyl-benzamide**,  $C_6H_5CON(CH_3)_2$ , m.p.  $78^\circ$  and  $41^\circ$ , respectively (Reid, Am. J. 45, 38).

**N-Methylol-benzamide**,  $C_6H_5CO \cdot NH \cdot CH_2OH$ , m.p.  $106^\circ$ , is obtained by condensing benzamide with formaldehyde, in the presence of alkaline condensing agents. When heated alone, or in aqueous solution, it readily breaks down into its components. It is oxidised by chromic acid to *formyl-benzamide*,  $C_6H_5CONHCHO$ , m.p.  $120^\circ$ . The latter gives 2,5-diphenyl-triazole with phenylhydrazine (Einhorn, Ann. 343, 223). The introduction of acyl residues into the  $NH_2$ -group of aromatic amides is described in Ger. Pat. 297,875. **Benzoyl-benzylamine**,  $C_6H_5CO \cdot NH \cdot CH_2C_6H_5$ , m.p.  $105^\circ$  (Bergmann, Ber. 26, 2273).

**Benzanilide**, *phenyl-benzamide*,  $C_6H_5CO \cdot NHC_6H_5$ , m.p.  $162-163^\circ$ , is formed: by the action of aniline on benzoyl chloride; by the action of aluminium chloride on phenylisocyanate and benzene (p. 289); by heating bromobenzene and benzamide with copper (Goldberg, Ber. 39, 1692); by heating benzophenone oxime,  $(C_6H_5)_2C:N \cdot OH$ , with concentrated sulphuric acid, acetyl chloride, or a mixture of hydrochloric acid and acetic acid to  $100^\circ$ , or with acetic acid alone to  $180^\circ$  (Beckmann, Ber. 20, 2581); and by passing a mixture of ethyl benzoate and aniline vapours over alumina or thoria heated to  $480^\circ$  (Mailhe, Caoutchouc, 1919, 16). For sodium-benzanilide, see Wheeler, Am. J. 28, 453.

When benzanilide is boiled with sulphur, *benzenyl-amino-thiophenol*, or  $\mu$ -

*phenyl-benzothiazol* is formed. *o*-, *m*-, and *p*-benzoyl-toluides,  $C_6H_5CONH \cdot C_6H_4CH_3$ , m.p. 131°, 135°, and 158°, respectively.

**Diphenyl-benzamide**,  $C_6H_5CON(C_6H_5)_2$ , m.p. 177°, is obtained from diphenylamine and benzoyl chloride, or from diphenyl-urea chloride by condensation with benzene and aluminium chloride (*Lehmann*, Ber. 20, 2119), or by heating with benzoic acid and pyridine (*Herzog*, Ber. 41, 636).

**Methylene-dibenzamide**,  $CH_2(NH \cdot CO \cdot C_6H_5)_2$ , m.p. 220°, is obtained by oxidation of hippuric acid with lead dioxide and dilute sulphuric acid, or dilute nitric acid. It is also obtained by the action of formaldehyde and hydrogen chloride on benzonitrile (*Pulvermacher*, Ber. 25, 311), and from benzamide by boiling with formaldehyde and dilute sulphuric acid (*Ernhorn*, Ann. 343, 226).

**Ethylidene-dibenzamide**,  $CH_3CH(NHCOC_6H_5)_2$ , m.p. 204° (*Nencki*, Ber. 7, 159).

**Ethylene-dibenzamide**,  $C_6H_5CO \cdot NH \cdot CH_2CH_2 \cdot NH \cdot COC_6H_5$ , m.p. 249°. When heated alone or with hydrochloric acid, this compound loses benzoic acid and gives ethylene-benzenyl-amidine (*Hofmann*, Ber. 21, 2334).

**Benzoyl isocyanate**,  $C_6H_5CON:CO$ , m.p. 26°, b.p. 88° (10 mm.), obtained by the action of silver isocyanate on benzoyl chloride, forms dibenzoyl-urea with water, and benzoyl-urethane,  $C_6H_5CONHCOOC_2H_5$ , m.p. 111°, with alcohol (*Billeter*, Ber. 36, 3218).

**Hippuric acid**, *benzoyl-glycoroll*,  $C_6H_5CO \cdot NH \cdot CH_2COOH$ , m.p. 187°, occurs in large quantities in the urine of herbivorous animals, such as the cow and the horse (*ἵππος*, horse, and *ὄρον* urine), and in small concentrations in human urine. When benzoic acid, cinnamic acid, and toluene are taken internally they are eliminated as hippuric acid. It can be obtained synthetically (1) by heating benzamide with monochloroacetic acid; (2) by the action of silver glycoroll on benzoyl chloride (*Curtius*, Ber. 15, 2740); (3) from benzoyl chloride, glycoroll, and sodium hydroxide (*Baum*, Physiol. Ch. 9, 465); (4) by heating benzoic anhydride with glycoroll (*Curtius*, Ber. 17, 1662); (5) from benzaldehyde and sodium aminoacetate, followed by oxidation (*Pauly*, Physiol. Ch. 99, 164).

*History*.—As far back as 1829, *Liebig* recognised that hippuric acid differed from benzoic acid, and gave the acid its present name, to indicate its origin. He established its composition in 1839. *Dessaignes* (1846) showed that it was decomposed to glycoroll and benzoic acid when boiled with concentrated alkalis or acids (J. pr. [1], 37, 244). In 1848, *Strecker* converted the acid into benzoyl-glycolic acid by acting on it with nitrous acid (Ann. 68, 54), and in 1853, *Dessaignes* synthesised hippuric acid from benzoyl chloride and zinc glycine (Ann. 87, 325).

Hippuric acid crystallises in rhombic prisms, and is soluble in 600 parts of cold water. It dissolves more readily in hot water, and in alcohol. It is decomposed slowly by boiling caustic soda, and more rapidly by mineral acids, into glycoroll and benzoic acid.

For other reactions of hippuric acid, see methylene-dibenzamide (above), and benzoyl-glycolic acid (p. 296). It condenses with aldehydes, *e.g.*, benzaldehyde, in the presence of sodium acetate and acetic anhydride, to form *benzoyl-amino-*

*cinnamic anhydride*,  $C_6H_5CH: \begin{array}{c} \diagup N=CC_6H_5 \\ \diagdown CO-O \end{array}$  (p. 467), an oxazolone, *azlactone*

of  $\alpha$ -benzoyl-amino-cinnamic acid (*Erlenmeyer*, Ann. 337, 265).

**Silver hippurate**,  $C_9H_8NO_3Ag$ . **Ethyl hippurate**, m.p. 60° (*Conrad*, J. pr. 15, 247), is converted by phosphorus pentachloride (2 mols.) into *hippuro-flavin*,  $C_{18}H_{16}O_4N_2$ , lemon-coloured crystals, m.p. above 300° (*Rügheimer*, Ber. 21, 3321; 26, 2324; Ann. 312, 81), and by benzaldehyde and sodium acetate into *benzoyl-amino-cinnamic ester* (*Erlenmeyer*, Ann. 275, 12). **Phenyl hippurate**, m.p. 104°,

gives *phenyl-anhydro-hippurate*, m.p. 42°, when boiled with phosphorus oxychloride (Weiss, Ber. 26, 2641).

Ethyl hippurate condenses with ethyl formate and sodium ethoxide to give **ethyl formyl-hippurate**,  $C_6H_5CO \cdot NH \cdot CH(CHO)CO_2C_2H_5$ , which is reduced by sodium amalgam to the **ethyl ester of benzoyl-serine**,  $C_6H_5CO \cdot NH \cdot CH(CH_2OH)CO_2C_2H_5$ , m.p. 80°. The latter is decomposed by sulphuric acid into benzoic acid and *dl*-serine. With phosphorus pentasulphide it gives **benzoyl-cysteine ester**,  $C_6H_5CONH \cdot CH(CH_2SH)CO_2C_2H_5$ , m.p. 185°. By hydrolysis of this compound with concentrated hydrochloric acid, *dl*-cysteine and its oxidation product, *dl*-cystine are obtained (Erlenmeyer, Ann. 337, 236). **Hippuryl chloride**,  $C_6H_5CONHCH_2COCl$ , decomp. at 125°, is obtained by the action of acetyl chloride and phosphorus pentachloride on hippuric acid. With diazomethane it gives *phenyl-*

*hydroxy-dihydro-metorazine*, m.p. 91°, 
$$\begin{array}{c} N=C(C_6H_5)-O \\ | \\ CH_2-CO-CH_2 \end{array} \quad \text{or} \quad \begin{array}{c} N=C(C_6H_5)-O \\ | \\ CH_2-C(OH)=CH \end{array}$$
 (Karrer, Helv. 8, 203).

**$\alpha$ -Hydroxy-hippuric acid**,  $C_6H_5CO \cdot NHCH(OH)COOH$ , melts at 145–150°, with effervescence, solidifies, and melts again at 208–213°, with decomp. It is obtained by brominating hippuric acid and acting on the product with water. When heated in water it breaks up into benzamide and glyoxylic acid. The latter gives a violet coloration with proteins and concentrated sulphuric acid, a reaction which therefore serves for the detection of hippuric acid (Haas, J. 101, 1254).

**Hippuronitrile**,  $C_6H_5CONHCH_2CN$ , m.p. 144°, is obtained from amino-acetonitrile and benzoyl chloride by the action of sodium hydroxide (Klages, Ber. 36, 1646). **Hippuryl-hydrazine**,  $C_6H_5CO \cdot NHCH_2CO \cdot NH \cdot NH_2$ , m.p. 162°, is obtained from the action of ethyl hippurate and hydrazine; cf. *hippuryl-phenyl-buzylene*, p. 165, and *hippurazide*, p. 303 (Curtius, J. pr. 52, 243).

*dl*-**Benzoyl-alanine**,  $C_6H_5CONH \cdot CH(CH_3)COOH$ , m.p. 166°, has been resolved into its optical isomerides by means of brucine (Fischer, Ber. 32, 2458). This compound, and **benzoyl- $\alpha$ -amino-isobutyric acid**,  $C_6H_5CONHC(CH_3)_2COOH$ , m.p. 198°, are readily converted into azlactones (oxazolones), when heated with

acetic anhydride. **Benzoyl-alanine-oxazolone**, m.p. 39°, 
$$\begin{array}{c} C_6H_5C=N \\ | \quad \diagup \\ O-C \quad CHCH_3 \\ || \\ O \end{array}$$

and **benzoyl- $\alpha$ -amino-isobutyric-oxazolone** (see Vol. IV), m.p. 34°, 
$$\begin{array}{c} C_6H_5C=N \\ | \quad \diagup \\ O-C \quad C(CH_3)_2 \\ || \\ O \end{array}$$
 Cf. the similarly constituted acyl-anthranilic acids.

Ammonia, aniline, or hydrochloric acid breaks the lactone ring and amides, anilides, or chlorides of the corresponding benzoyl-amino-acids are formed. Similarly,  $\omega$ -amino-acids are attached with the formation of benzoylated dipeptides, e.g., *benzoyl-alanyl-glycocoll*,  $C_6H_5CONH \cdot CH(CH_3)CONHCH_2COCH_3$ , and *benzoyl-alanyl-alanine*,  $C_6H_5CONH \cdot CH(CH_3)CONH \cdot CH(CH_3)COOH$ , etc. (Mohr, J. pr. 81, 49, 473).

**Benzoyl-aspartic acid**, see Pauly, Ber. 43, 661.

**Benzoyl-urea**,  $C_6H_5CONHCONH_2$ , m.p. 215°, is obtained from urea by the action of benzoyl chloride or anhydride. With chlorine it gives benzoyl-chloro-urea,  $C_6H_5CO \cdot NC(ONH_2)$ , m.p. 157° (decomp.). It is also obtained from benzoyl-cyanamide. Alkali causes ring-closure, and the formation of a compound,

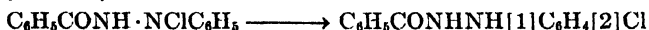
not yet isolated, but believed to be 
$$\begin{array}{c} C_6H_5 \cdot CO \cdot N \\ | \\ HN \end{array} \diagup CO$$
, which gives **benzoyl-car-**

**bohydrazide**,  $C_6H_5CONHNHCONHNH_2$ , m.p. 186°, with hydrazine (Diels, Ber. 45, 874, 2437).

**7. ACID HYDRAZIDES.** **Benzoyl-hydrazine**,  $C_6H_5CONHNH_2$ , m.p. 116°, has been obtained by the action of hydrazine hydrate on ethyl benzoate, and by heating hydrazine benzoate (Curtius, Ber. 35, 3240). In alkaline solution it undergoes auto-reduction, giving first benzyldene-benzoyl-hydrazine,  $C_6H_5CONHN:CHC_6H_5$  (see below), and then benzalazine (p. 272) (Curtius, Ber. 33,

2561). When an excess of hydrazine acts on ethyl benzoate, *sym*-dibenzoyl-hydrazine,  $(C_6H_5CONH)_2$ , m.p.  $238^\circ$ , is formed, which is also obtained by the action of an alkaline solution of hydrazine on benzoyl chloride (*Pellizzari*, *Lincei* 8, I, 327). When boiled with alcoholic potash it gives a potassium salt,  $(C_6H_5CO)_2N_2HK$ ; the corresponding silver salt gives *azo*-dibenzoyl,  $(C_6H_5CO)_2N_2$ , m.p.  $118^\circ$ , with iodine (*Stollé*, *Ber.* 33, 1769). Tri- and tetra-benzoyl-hydrazines, m.p.  $206^\circ$  and  $238^\circ$ , respectively, are obtained by continued benzylation of dibenzoyl-hydrazine (*Freundler*, *Bull.* [3], 31, 616).

*sym*-Benzoyl-phenylhydrazine, m.p.  $168^\circ$  (*Just*, *Ber.* 19, 1203) on oxidation with mercuric oxide or nitrous acid, is converted into benzoyl-azo-benzene,  $C_6H_5CON_2C_6H_5$ , red prisms, m.p.  $80^\circ$  (*Ponzo*, *Gazz.* 39, I, 596); the latter forms an addition product with hydrogen chloride, which rearranges to *o*-chlorophenyl-benzoyl-hydrazine,



(*Hantzsch*, *Ber.* 30, 319).

*as*-Benzoyl-phenylhydrazine, m.p.  $70^\circ$  (*Widman*, *Ber.* 26, 945). Dibenzoyl-phenylhydrazine,  $C_6H_5 \cdot CO \cdot NC_6H_5 \cdot CHCO_2C_6H_5$ , m.p.  $177^\circ$ . Benzylidene-benzoyl-hydrazine,  $C_6H_5CO \cdot NHN : CHC_6H_5$ , m.p.  $203^\circ$ , is obtained from benzoyl-hydrazine and benzaldehyde, or by the action of benzoyl chloride on benzalazine (p. 272) (*Minum*, *Gazz.* 29, II, 377). The corresponding silver salt,

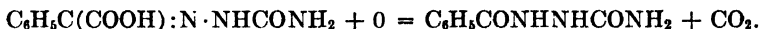
$C_6H_5CONAgN : CHC_6H_5$ , gives *diphenyl-furodiazole*,  $C_6H_5C \begin{array}{c} \diagup N \diagdown \\ \diagdown O \diagup \end{array} CC_6H_5$ , with

iodine, and *diphenyl-benzoyl-dihydrofurodiazole*,  $C_6H_5C \begin{array}{c} \diagup N \diagdown \\ \diagdown N \diagup \\ \diagdown O \diagup \end{array} \begin{array}{c} \diagup N \diagdown \\ \diagdown CH \diagup \end{array} \begin{array}{c} \diagup N \diagdown \\ \diagdown COC_6H_5 \diagup \end{array}$ , with

benzoyl chloride (*Stollé*, *J. pr.* 70, 393).

Phenylacetic-hydrazide, m.p.  $116^\circ$ ; hydrocinnamic hydrazide, m.p.  $103^\circ$ .

7a. **ACID SEMICARBAZIDES.** These are formed when semicarbazones of aromatic  $\alpha$ -keto-acids are oxidised with a solution of iodine in potassium iodide containing sodium carbonate:

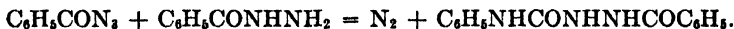


Benzoyl-semicarbazide, m.p.  $240^\circ$ ; phenacetyl-semicarbazide, m.p.  $156^\circ$ .  $\beta$ -Phenyl-propionyl-semicarbazide, m.p.  $192^\circ$ . By the action of semicarbazide on benzoic anhydride, an "acid benzoyl-semicarbazide," m.p.  $225^\circ$ , has been obtained, but it differs from the above-mentioned compound, and the enol formula,  $C_6H_5C(OH) : N \cdot NHCONH_2$ , has been assigned to it (*Bougault*, *C.r.* 163, 305; 164, 820).

8. **ACIDYL AZIDES.** Benzoyl azide, benzoyl azimide,  $C_6H_5CON_3$ , m.p.  $29^\circ$ , obtained by the action of nitrous acid and acetic acid on benzoyl-hydrazine, or by the action of potassium azide on benzoyl chloride in moist acetone (*Powell*, *Am.* 51, 2436), smells strongly like benzoyl chloride. It is partially volatile with steam without decomposition, and explodes on heating, but not violently. It is insoluble in water, but dissolves fairly readily in alcohol, and freely in ether. It has a neutral reaction. It is decomposed by boiling alkalis to potassium azide and benzoic acid (*Curtius*, *Ber.* 23, 3029). On heating in benzene it breaks down smoothly into nitrogen and phenyl-isocyanate:



(*Schroeter*, *Ber.* 42, 2339). When heated with alcohol or water it undergoes analogous reactions, nitrogen being lost and derivatives of phenyl isocyanate, such as *phenyl-urethane*,  $C_6H_5NHCOOC_2H_5$ , and *carbanilide*,  $CO(NHC_6H_5)_2$ , formed. When boiled with acid hydrazides, semicarbazides are formed:



When acted upon with bromine, a bromine addition product of phenyl isocyanate is formed (*Curtius*, *J. pr.* 52, 215; 53, 513). Substituted benzazides, such as the *o*-, *m*-, and *p*-nitro-benzazides, m.p.  $36^\circ$ ,  $68^\circ$ , and  $69^\circ$ , and *p*-bromo-benzazide, m.p.  $46^\circ$ , behave similarly (*Portner*, *J. pr.* 58, 190). Phenylacetic-azide,



$C_6H_5CH_2CON$ , and hydrocinnamic-azide,  $C_6H_5CH_2CH_2CON_3$ , give the urethanes of benzylamine and phenyl-ethylamine, respectively, with alcohol (*Jordan*, J. pr. 64, 297). The azides can also be obtained by the action of diazonium salts on the acid hydrazides.

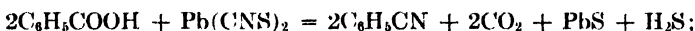
**Hippurazide**,  $C_6H_5CO \cdot NH \cdot CH_2 \cdot CO \cdot N_3$ , m.p.  $98^\circ$ , is formed by the action of sodium nitrite and acetic acid on hippuryl-hydrazine. It is decomposed by mineral acids, alkalis, ammonia, and amines, with the elimination of hydrazoic acid. When boiled with alcohols, and with water, nitrogen is evolved, and **hippenyl-urethanes**,  $C_6H_5CONHCH_2NHCOOR$ , and **dihippenyl-urea**,  $(C_6H_5CONHCH_2NH)_2CO$ , m.p.  $246^\circ$ , are formed (*Curtius*, J. pr. 52, 243; 37, 513). When hippurazide acts on glyceroll, glycyl-glycine, alanine, etc., benzoyl derivatives of di- and poly-peptides, such as  $C_6H_5CONHCH_2CONHCH_2COOH$ ,  $C_6H_5CONHCH_2CONHCH_2CONHCH_2CONHCH_2COOH$ ,  $C_6H_5CONHCH_2CONHCH_2CONHCH_2CONHCH_2CONHCH_2COOH$ , etc., are formed (*Curtius*, J. pr. 70, 57).

## B. BENZENYL COMPOUNDS

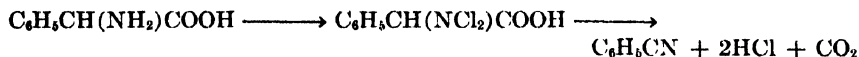
These comprise groups sections 9 to 30, dealt with below.

### 9. Nitriles of the Aromatic Monocarboxylic Acids

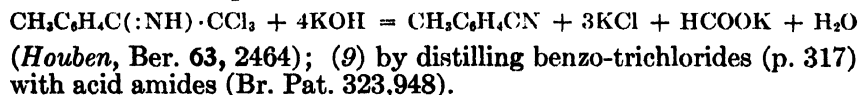
The aromatic nitriles are connected by numerous reactions with the principal classes of aromatic derivatives. They are produced, like the aliphatic nitriles (1) from the corresponding ammonium salts; (2) from the corresponding acid amides by dehydration with phosphorus pentoxide, phosphorus pentachloride, or thionyl chloride (*Michaelis*, Ann. 274, 312); (3) by the action of bromine and caustic alkali on primary phenyl alkylamines or by catalytic dehydrogenation (*Sabatier*, C.r. 165, 224); (4) from the aldoximes, by the action of acetyl chloride, or acetic anhydride. They may also be obtained (5) by distilling aromatic monocarboxylic acids with potassium thiocyanate, or, better, lead thiocyanate (*Kruess*, Ber. 17, 1766):



(6) by passing the vapours of aldehydes, esters, or acid chlorides with ammonia or primary aliphatic amines over alumina or thoria, heated to  $400-500^\circ$  (*Mailhe*, C.r. 166, 215; 170, 813; Bull. 23, 380; Caoutchouc, 1918); (7) by the action of sodio-*p*-toluene-sulphochloroamide on  $\alpha$ -amino-phenylacetic acids:



(*Dakin*, Biochem. J. 10, 319); (8) by the fission of trichloro-acetiminocompounds obtained from benzene hydrocarbons and trichloro-acetonitrile in the presence of aluminium chloride:

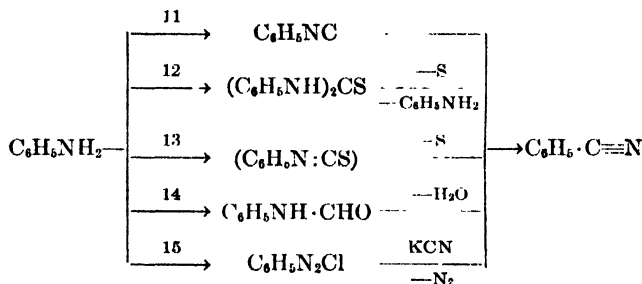


**Nuclear syntheses.** (10) The direct replacement of halogen by the cyanogen group is effected by passing chloro- or bromo-benzene over strongly heated potassium ferrocyanide, and when benzene hydrocarbons, halogenated in the ring, but containing no *o*- or *p*- nitro-group, are heated with finely divided or dissolved metallic cyanides at temperatures up to  $350^\circ$  (Ger. Pat. 293,094). Phenyl-carbinol

chlorides, such as  $C_6H_5CH_2Cl$ , react readily with potassium cyanide, more readily indeed than the alkyl halides, forming phenyl-aliphatic nitriles.

Nuclear hydrogen atoms are directly replaced by the cyanogen group (a) when cyanogen gas is passed into the boiling hydrocarbon mixed with aluminium chloride (*Desgrez*, Bull. [3] 13, 734); (b) by the action of mercury fulminate,  $(C:NO)_2Hg$  on benzene and anhydrous aluminium chloride, benzonitrile is formed in 80% yield; if hydrated aluminium chloride is used, benzaldoxime is formed (*Scholl*, Ber. 36, 10). For the action of chlorine and bromine cyanide on benzene hydrocarbons in the presence of aluminium chloride, see *Scholl*, Ber. 33, 1052).

The nitriles are also closely related to the anilines, sulphonic acids, and phenols. Thus, aniline yields: (11) phenyl-carbylamine, which changes into the isomeric nitrile when heated; (12) diphenyl-thiourea, which gives the nitrile when heated with zinc; (13) phenyl-mustard oil, which gives the nitrile when sulphur is removed from it by means of copper; (14) formanilide, which gives the nitrile when distilled with concentrated hydrochloric acid, or zinc dust (*Goussiorowsky*, Ber. 17, 73), or when its vapour, or that of aniline formate, is passed over activated carbon, heated to  $425^\circ$  (Ger. Pat. 482,943); (15) phenyl-diazonium chloride, which gives the nitrile when treated with potassium cyanide and copper sulphate (*Roshdestvenski*, Zhurnal, 1933, 6, 274).



For the theoretical importance of method (15), see p. 13. (16) Nitriles are also obtained from alkali benzene-sulphonates and (17) from triphenyl phosphates, by distillation with potassium cyanide or ferrocyanide. (18) Alkyl-benzyl cyanides are also produced from sodium-benzyl cyanide and alkyl halides,  $C_6H_5CHNa \cdot CN + C_2H_5I = C_6H_5CH(C_2H_5)CN + NaI$  (see below).

**Properties and reactions.**—The benzonitriles are liquids with an agreeable smell, or solids with low melting points. Their reactions are very numerous, but it may be mentioned that boiling alkalis or acids convert them into the corresponding aromatic acids, while nascent hydrogen, best from sodium and alcohol, reduces them to primary amines. With hydriodic acid, they give *amide iodides*. They combine with alcohols and hydrogen chloride to give *imidoethers*, with ammonia and anilines to give *amidines*, and with hydroxylamine to give *amidoximes*.

**Benzonitrile, phenyl cyanide**,  $C_6H_5CN$ , m.p.  $-12^\circ$ , b.p.  $191^\circ$ ,

$d_0$  1.023, is isomeric with phenyl-carbylamine (p. 90), and is best obtained from benzene-sulphonic acid by method (16), or from benzoic acid by method (5). It is an oil, with an odour resembling that of oil of bitter almonds. When it is dissolved in fuming sulphuric acid, or boiled with sodium, or acted upon by other condensing agents, benzonitrile polymerises to *cyaphenine*,  $C_3N_3(C_6H_5)_3$ . When this is nitrated, the product is almost exclusively *m*-nitro-benzonitrile (p. 319).

With chlorine, it yields two hexachlorides,  $\alpha$ - m.p.  $156^\circ$ ,  $\beta$ - m.p.  $197^\circ$ , and a *p*-chloro-hexachloride, m.p.  $206^\circ$  (*van der Linden*, *Rec.* 53, 45). The isocyanide, which is also formed, is extracted with warm 50% sulphuric acid (*Gibson*, *Org. Synth.* 16, 89).

*Aryl cyanides.* *o*-, *m*-, *p*-**Tolunitriles**, *cyano-toluenes*,  $CH_3C_6H_4CN$ , m.p.  $-13^\circ$ ,  $-23^\circ$ ,  $29^\circ$ ; b.p.  $203^\circ$ ,  $213^\circ$ ,  $218^\circ$ , respectively. When catalytically reduced, mixtures of *o*-, *m*-, and *p*-tolualdehydes and toluidines are formed. *p*-**Xylic nitrile**, b.p.  $231^\circ$  (*Kreysler*, *Ber.* 18, 1712); 1,3-Xylic-4-nitrile, m.p.  $24^\circ$ , b.p.  $222^\circ$  (*Hunrichsen*, *Ber.* 21, 3082). **Cumonnitrile**,  $(CH_3)_2CH[4]C_6H_4[1]CN$ , b.p.  $244^\circ$ .

*Phenyl-aliphatic nitriles.* **Benzyl cyanide**, *phenyl-acetonitrile*,  $C_6H_5CH_2CN$ , m.p.  $-24.6^\circ$ , b.p.  $233^\circ$ ,  $d_4^{20}$  1.018, is isomeric with the three tolunitriles. It is obtained from benzyl mustard oil occurring in *Tropaeolum majus* and *Lepidium sativum* (p. 259) (*Gudamer*, *Ber.* 32, 2335), and synthetically from benzyl chloride and potassium cyanide. It is hydrolysed to phenylacetic, or  $\alpha$ -toluic acid (p. 293), and reduced to  $\beta$ -phenyl-ethylamine (p. 258). When nitrated, the chief product is *p*-nitrobenzyl cyanide, m.p.  $116^\circ$ . *p*-**Bromobenzyl cyanide**, m.p.  $29^\circ$ , b.p.  $130^\circ$  (12 mm.), is obtained from benzyl cyanide by the action of bromine vapour. It causes violent irritation of the eyes and nose.

As in acetoacetic and malonic esters, the hydrogen of the  $CH_2$  group linked to the activating  $C_6H_5$  and CN groups is very readily replaced. Thus, sodium ethoxide gives monosodio-benzyl cyanide, which reacts with alkyl halides to give alkyl-benzyl cyanides (cf. method 18, p. 305), and with esters to give cyanoketones,  $Ar \cdot CH(CN)CO \cdot R$  (*Meyer*, *Ber.* 21, 1291; *Rossolyma*, *Ber.* 22, 1238; *Buddeberg*, *Ber.* 23, 2070; *Reid*, *Am. J.* 45, 38).

Benzyl cyanide reacts as follows: with sodium ethoxide and nitrous acid to give *iso-nitrosobenzyl cyanide*,  $C_6H_5C(:NOH)CN$ ; with sodium ethoxide and ethyl nitrate to give *ac-nitrosobenzyl cyanide*,  $C_6H_5C(:NOOH)CN$ ; with sodium ethoxide and benzaldehyde to give  $\alpha$ -phenyl-cinnamic nitrile,  $C_6H_5C(CN):CH \cdot C_6H_5$  (*Frost*, *Ann.* 250, 156). Like sodio-malonic ester, it adds on to  $\alpha, \beta$ -unsaturated esters and ketones. Catalytic hydrogenation of nitrile at low pressure converts them into mono- and di-arylamines; thus, benzonitrile is converted into mono- and di-benzylamine, and benzyl cyanide into mono- and di-phenyl-ethylamine (*Grignard*, *Bull.* 49, 522). When treated with chlorobenzene and sodium, benzonitrile gives sodium benzophenone-imide,  $(C_6H_5)_2C:N \cdot Na$ , and when this is acted upon by water it is converted into benzophenone by the oxygen of the air, into benzophenone oxime, and by iodine into diphenyl-ketazine,  $(C_6H_5)_2C:N \cdot N:C(C_6H_5)_2$  (*Morton*, *Am.* 53, 2769).

**Methyl-benzyl cyanide**, *o*-, *m*-, and *p*-**tolyl-acetonitriles**,  $CH_3 \cdot C_6H_4 \cdot CH_2CN$ , b.p.  $244^\circ$ ,  $241^\circ$ ,  $243^\circ$ ; m.p. of *p*-form- $18^\circ$  (*Radiszewski*, *Ber.* 18, 1281; *Paepcke*, *Ber.* 21, 1331).

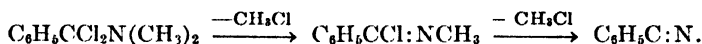
**$\beta$ -Phenyl-propionitrile**, *hydrocinnamic nitrile*,  $C_6H_5CH_2CH_2CN$ , b.p.  $261^\circ$  (corr.), has been extracted from *Nasturtium officinale*, by steam distillation.  $\alpha$ -**Phenyl-propionitrile**, *hydratropic nitrile*,  $C_6H_5CH(CH_3)CN$ , b.p.  $231^\circ$ , is prepared by the action of phosphorus oxychloride on the acid chloride (*Kao*, *J. Chin.* 2, 240; see also *Meyer*, *Ann.* 250, 123; *Janssen*, *Ann.* 250, 137).

#### 10. Amido Halides. 11. Imidochlorides. 12. Phenylhydrazido-imidochlorides

**Benzamido-chloride**,  $C_6H_5CCl_2NH_2$ , is formed when gaseous hydrogen chloride is passed into an ether solution of benzonitrile (*Pinner*, *Ber.* 10, 1891).

It is probably the primary product when phosphorus pentachloride acts on benzamide, although under the conditions of this reaction, it partly breaks down into benzonitrile and hydrogen chloride, and partly combines with the phosphorus oxychloride, formed during the reaction, to give phosphorus compounds, such as  $C_6H_5CCl_2NHPOCl$ , and  $C_6H_5CCl:NPOCl$  (Titherley, J. 95, 1143). **Benz-amido-bromide**,  $C_6H_5CBr_2NH_2$ , m.p.  $70^\circ$  (Engler, Ann. 149, 307). **Benzamido-iodide**,  $C_6H_5CI_2NH_2$ , b.p.  $140^\circ$  (decomp.) (Biltz, Ber. 25, 2536), is formed when benzonitrile is poured into concentrated hydriodic acid.

**Dimethyl-benzamide chloride**,  $C_6H_5CCl_2N(CH_3)_2$ , m.p.  $36^\circ$ , is obtained from the amide by the action of carbonyl chloride or phosphorus pentachloride. When heated, the dialkyl-benzamide chlorides lose one or two molecules of alkyl chloride, and form alkyl-benzimide chlorides and benzonitrile. The latter partly polymerises to cyaphenine (p. 309) (Braun, Ber. 37, 2812).



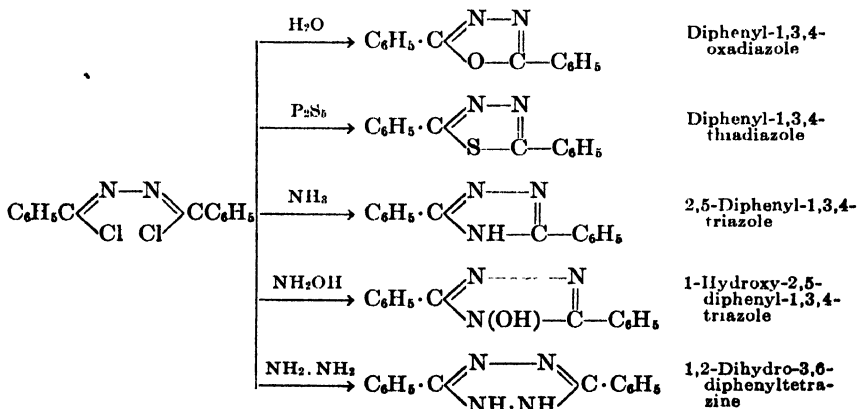
This reaction is used in the degradation of secondary cyclic bases, cf. piperidine.

**Benzanilide chloro-iodide**,  $C_6H_5CCH:NHC_6H_5$ , m.p.  $106^\circ$  (decomp.), is obtained by the action of hydriodic acid on benzanilide imidochloride (Lander, J. 85, 1695), and **methyl-benzimido-chloride**,  $C_6H_5CCl:NCH_3$ , is obtained by the action of phosphorus pentachloride on methyl-benzamide.

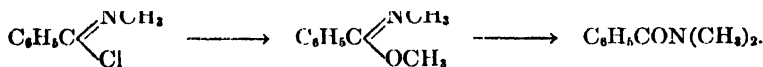
**Benzanilide imidochloride**,  $C_6H_5CCl:NCC_6H_5$ , m.p.  $40^\circ$ , b.p.  $310^\circ$ , is obtained from benzanilide by the action of phosphorus pentachloride (Wallach, Ann. 184, 79), or thionyl chloride, or by the action of phosphorus pentachloride on benzo-phenone oxime,  $(C_6H_5)_2C:N:OH$ ; an atomic rearrangement of the chloride  $(C_6H_5)_2C:NCl$  occurs in this reaction. It is decomposed by water or alcohol into benzanilide and hydrogen chloride. It is converted into 1,5-diphenyl-tetrazole by sodium azide. For other reactions of benzanilide-imidochloride, see benzimido ether and thio-benzanilide (p. 308). With sodio-acetoacetic ester or sodio-malonic ester, *anti*-benzenyl compounds are formed. These are derivatives of  $\beta$ -keto-acids, and are converted into phenyl-quinoline-carboxylic acids on heating.

**Benzo-phenyl-hydrazide imidochloride**,  $C_6H_5CCl:N:NH \cdot C_6H_5$ , m.p.  $131^\circ$ , is formed when alcohol acts upon the reaction product of phosphorus pentachloride and *sym*-benzoyl-phenylhydrazine,  $C_6H_5CCl:N \cdot N(C_6H_5)POCl_2$  (Pechmann, Ber. 27, 2122).

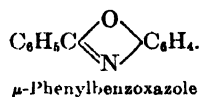
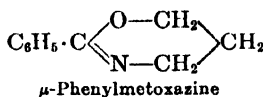
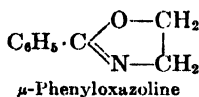
**Dibenzo-hydrazide chloride**,  $C_6H_5CCl:N \cdot N:ClCC_6H_5$ , m.p.  $123^\circ$ , is obtained by the action of phosphorus pentachloride on *sym*-dibenzoyl-hydrazine. It can readily be converted into heterocyclic compounds. Thus, (1) on boiling with water it gives diphenyloxadiazole; (2) with phosphorus pentasulphide, it gives diphenylthiadiazole; (3) with ammonia or primary amines it gives diphenyltriazole; (4) with hydroxylamine, *N*-hydroxy-diphenyltriazole; (5) with hydrazine, diphenyl-dihydro-tetrazine (Stollé, J. pr. 73, 227):



**13. IMIDO-ETHERS OF AROMATIC CARBOXYLIC ACIDS.** The hydrochlorides of imido-ethers are formed by the action of hydrochloric acid on alcoholic solutions of nitriles (Pinner, Ber. 16, 1654; 23, 2917; Glock, Ber. 21, 2650). Their hydriodides can be prepared by heating acid amides with alkyl iodides and cuprous oxide, lead oxide, or potassium carbonate (Matsui, Mem. Kyoto, 1910). Their methyl sulphates are obtained by addition of dimethyl sulphate to primary and secondary acid amides. The hydrochlorides of the imido-ethers are decomposed by water giving esters and ammonium chloride. Benzalkyl-imidochlorides (p. 307) change into benzalkyl-imido-ethers with sodium alcoholates. The benzalkyl-imidochlorides are converted into tertiary benzamides by the action of alkyl iodides, or by heating (Lauder, J. 83, 320):



Sodium amalgam reduces benzimido-ether in acid solution to benzaldehyde (Henle, Ber. 35, 3039). With ammonia the benzimido-ethers give *benzamidine*, with hydroxylamine, *benzamidozime*; with hydrazine, *benzenyl-hydrazine*. The following substances are cyclic imido-ethers of aromatic carboxylic acids:



**Benzimido-methyl ether**,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{OCH}_3$ , b.p.  $96^\circ$  (13 mm.), and **benz-imido-ethyl ether**,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{OC}_2\text{H}_5$ , b.p.  $102^\circ$  (15 mm.), are oils, precipitated from their hydrochlorides by sodium carbonate solution. The ethyl ether is also obtained by the action of silver benzamide on ethyl iodide. In a similar way, silver dibenzamide gives with ethyl iodide, **benzoyl-benzimido-ethyl ether**  $\text{C}_6\text{H}_5\text{C}(\text{NCOC}_6\text{H}_5)\text{OC}_2\text{H}_5$ , m.p.  $65^\circ$  (Wheeler, Am. Ch. J. 20, 64). **N-Methyl-benzimido-methyl ether**,  $\text{C}_6\text{H}_5\text{C}(\text{NCH}_3)\text{OCH}_3$ , b.p.  $94^\circ$  (12 mm.).

**14. THIOAMIDES OF THE AROMATIC ACIDS.** **Thiobenzamide**,  $\text{C}_6\text{H}_5\text{CSNH}_2$ , or  $\text{C}_6\text{H}_5\text{C}(\text{SH})\text{NH}_2$ , m.p.  $116^\circ$ , is produced by passing hydrogen sulphide into an alcoholic solution of benzonitrile, mixed with ammonia (Gabriel, Ber. 23, 158), and when benzylamine is heated to  $180^\circ$  with sulphur (Wallach, Ann. 259, 304). Zinc and hydrochloric acid convert it into benzylamine, iodine

into diphenyl-1,2,4-thiadiazole,  $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \diagup \text{N}-\text{S} \\ \diagdown \text{N}=\text{C} \cdot \text{C}_6\text{H}_5 \end{array}$  (Hofmann, Ber. 25, 1588),

ethylene dibromide into  $\mu$ -phenyl-thiazoline (see below), trimethylene bromide into  $\mu$ -phenyl-metathiazine (see imido-thio-ethers), and ethylene diamine into

**benzenyl-ethylene diamine**, or **2-phenyl-imidazoline**,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \diagup \text{NH}-\text{CH}_2 \\ \diagdown \text{N}-\text{CH}_2 \end{array}$  (Forssell,

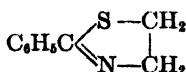
Ber. 25, 2134). **Methyl-thio-benzamide**,  $\text{C}_6\text{H}_5\text{CSNHCH}_3$ , m.p.  $79^\circ$ , is obtained from phenyl-magnesium bromide and methyl-mustard oil (Sachs, Ber. 37, 877).

**Thio-benzanilide**,  $\text{C}_6\text{H}_5\text{CSNH} \cdot \text{C}_6\text{H}_5$ , m.p.  $98^\circ$ , consists of yellow prisms or plates. It is formed: (1) by the action of hydrogen sulphide on benzenyl-phenyl-amidine at  $100^\circ$ ; (2) by the action of carbon disulphide on this substance at  $110^\circ$ , thiocyanic acid being formed at the same time (Bernthsen, Ann. 192, 29); (3) by the action of hydrogen sulphide on benzanilide chloride; (4) by the action of phosphorus pentasulphide on benzamide; (5) by the interaction of phenyl-mustard oil, benzene, and aluminium chloride (Friedmann, Ber. 25, 3525; Gattermann, J. pr. 59, 572); (6) by the action of phenyl-magnesium bromide on phenyl-mustard oil (Sachs, Ber. 36, 587). When heated or oxidised it is converted into benzenyl-amino-thiophenol. When methylated with dimethyl sulphate and sodium hydroxide it gives **3-methyl-thiobenzanilide**,  $\text{C}_6\text{H}_5\text{N}:\text{C}(\text{C}_6\text{H}_5)\cdot\text{SCH}_3$ , m.p.  $63-64^\circ$ . **N-Methyl-thiobenzanilide**,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{CSC}_6\text{H}_5$ , m.p.  $90-91^\circ$ , is produced by the action of phosphorus sulphide on methyl-benzanilide (obtained by the action of methyl-aniline on benzoyl chloride) (May, J. 103, 2272).

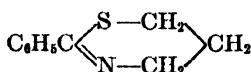
**Selenium benzamide**,  $\text{C}_6\text{H}_5\text{CS}_2\text{NH}_2$ , m.p.  $102^\circ$ , golden needles, is obtained

from benzonitrile and hydrogen selenide. It is oxidised by iodine to **diphenyl-1,2,4-selenadiazole**,  $C_6H_5C \begin{smallmatrix} N-Se \\ N=C \end{smallmatrix} C_6H_5$  (Becker, Ber. 37, 2550).

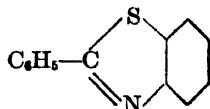
**15. IMIDO-ETHERS OF THE AROMATIC CARBOXYLIC ACIDS.** These are obtained as hydrochlorides from nitriles, mercaptans, and hydrochloric acid (cf. imido-ethers). The following compounds must be regarded as cyclic imido-thio-ethers of benzoic acid:



$\mu$ -Phenylthiazoline



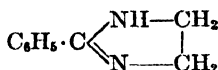
$\mu$ -Phenylmetathiazine



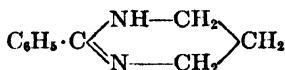
$\mu$ -Phenylbenzothiazole

**Benzimido-thio-ethyl-ether**,  $C_6H_5C(NH)SC_2H_5$ , is an oil. It readily breaks down into benzonitrile and mercaptan (Bernthsen, Ann. 197, 348). By heating sodium xanthogenates with benzalkyl-imidochlorides in benzene solution, the so-called imido-xanthides, which possess an intense red colour, are formed. **Benzo-phenyl-imido-ethyl xanthide**,  $C_6H_5C(NC_2H_5)SCSOC_2H_5$ , m.p.  $98^\circ$ , garnet-red prisms (Tschugaeff, Ber. 35, 2470). **Benzimido-thio-phenyl ether**,  $C_6H_5C(NH)SC_6H_5$ , m.p.  $48^\circ$  (Autenrieth, Ber. 36, 3465).

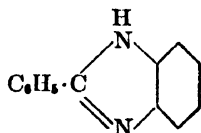
**16. AMIDINES OF AROMATIC MONOCARBOXYLIC ACIDS** are obtained by the action of ammonia or ammonium bases on nitriles, imido-ethers, imidochlorides, and thioamides. The cyclic amidines correspond to the cyclic imido-ethers and imido-thio-ethers:



$\mu$ -Phenylimidazoline



$\mu$ -Phenyltetrahydropyrimidine



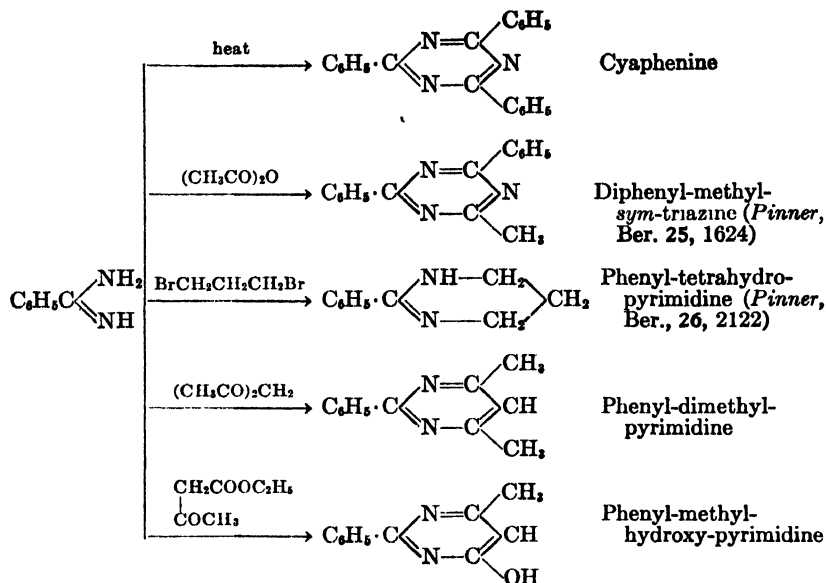
$\mu$ -Phenylbenzimidazole

**Benzamidine**,  $C_6H_5 \cdot C \begin{smallmatrix} NH_2 \\ NH \end{smallmatrix}$ , m.p.  $75-80^\circ$ , is formed from its hydrochloride,

$C_7H_7N_2 \cdot HCl + 2H_2O$ , consisting of glassy crystals m.p.  $72^\circ$  (cryst.),  $169^\circ$  (anhydrous) (Lossen, Ann. 265, 130).

**Silver salt**,  $C_6H_5C(=NAg)NH_2$ . Benzamidine is a stronger base than ammonia. When acted upon by hydroxylamine, an amidoxime is formed, the NH group being converted into N(OH). Benzamidine reacts as follows: with phenyldiazonium chloride it gives *benzamidine-diazobenzene* (see below); with benzaldehyde, **benzalbenzamidine**, m.p.  $175^\circ$  (Ber. 34, 3029); with phenyl isocyanate, **benzenyl-diphenyl-diureide**,  $C_6H_5C(:NCONHC_6H_5) \cdot NHCO \cdot NHC_6H_5$ , m.p.  $172^\circ$ ; with phenyl mustard oil, **benzamidine-phenyl-thiourea**,  $C_6H_5 \cdot C(:NH) \cdot NH \cdot CS \cdot NH \cdot C_6H_5$ , m.p.  $125^\circ$ ; with ethyl chlorocarbonate, **benzamidine-urethane**,  $C_6H_5 \cdot C(:NH) \cdot NHCOOC_2H_5$ , m.p.  $58^\circ$ , which gives *diphenyl-hydroxy-sym-triazine* when heated; with phosgene, **dibenzamidine-urea**,  $CO[NH \cdot C(:NH) \cdot C_6H_5]_2$ , m.p.  $289^\circ$ , and *diphenyl-hydroxy-sym-triazine*. The action of nitrous acid on benzamidine is very remarkable, *benzenyl-dihydroxy-tetrazotic acid* (see below) being formed.

**Hetero-ring formation with benzamidine.**—When benzamidine is heated alone it is converted into *cyaphenine*; when heated with acetic anhydride it gives *diphenyl-methyl-sym-triazine*; with trimethylene bromide, *trimethylene-benzamidine*, or *mu-phenyl-tetrahydro-pyrimidine*; with acetyl-acetone, *phenyl-dimethyl-pyrimidine*; with acetoacetic ester, *phenyl-methyl-hydroxy-pyrimidine* (Vol. IV).



Many other amidines, and numerous alkyl, phenyl, and benzyl substitution products of the simple amidines are known. Disubstituted cyanamides give amidines disubstituted in the amino-group by interaction with Grignard reagents (Adams, Am. 38, 2768). As will be seen from the above description, the amidines are unusually reactive substances, of which the investigation has contributed much to the chemistry of nitrogen-carbon ring systems. **Phenyl-benzamidine**,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NHC}_6\text{H}_5$ , m.p.  $114^\circ$ , is obtained by the action of sodium on a mixture of benzonitrile and aniline (Walther, J. pr. 67, 445). For the acylation of phenyl-benzamidine and the reaction mechanism see *Fransesconi*, Gazz. 32, II, 467. **Diphenyl-benzamidine**,  $\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_5)\text{NHC}_6\text{H}_5$ , m.p.  $144^\circ$ , is a chromogen, giving yellow dyes when amino-groups are introduced (Noelting, C. 1898, II, 1049). **Dibenzyl-benzamidine**, m.p.  $70-71^\circ$ , has been prepared from dibenzylcyanamide and phenyl-magnesium bromide, the hydrobromide, m.p.  $211.5^\circ$ , being formed intermediately (Adams, Am. 38, 2768). **Trialkyl-benzamidines**, see *Braun*, Ber. 37, 2678. For amidines of pharmacological interest, see *Easson* and *Pymn*, J. 1931, 2991.

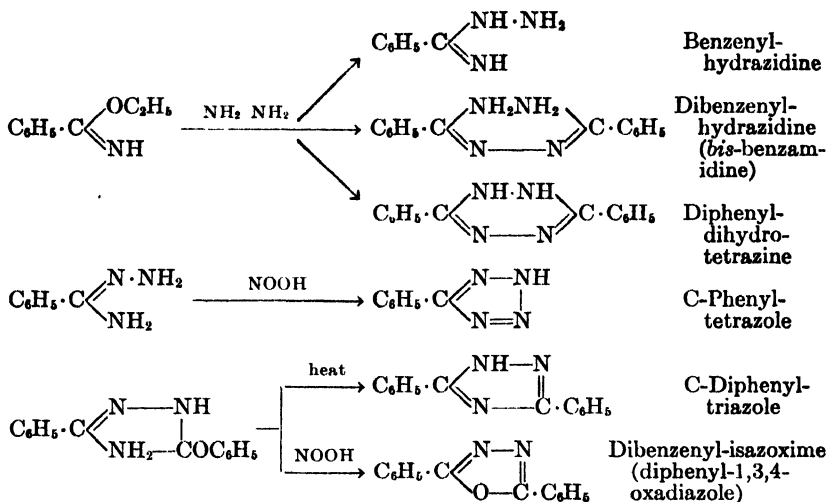
**17. DIHYDROXY-TETRAZOTIC ACIDS.** Free **benzenyl-tetrazotic acid**,  $\text{C}_6\text{H}_5\text{C} \begin{array}{c} \text{N}=\text{NOH} \\ \text{N}-\text{NO} \end{array}$ , is unknown. Its benzamidine salt, m.p.  $178^\circ$ , is formed by the action of nitrous acid on benzamidine. The potassium salt is reduced by sodium amalgam to **benzenyl-hydroxy-tetrazotic acid**  $\text{C}_6\text{H}_5\text{N}_4\text{O} + \text{H}_2\text{O}$ , m.p. (anhyd.)  $175^\circ$ , with explosion, and **benzenyl-tetrazotic acid** (*Lossen*, Ann. 263, 265, 129). These compounds belong to the class of heterocyclic *tetrazoles*, or *pyro-triazoles* (Vol. IV).

**18. HYDRAZIDINES, OR AMIDRAZONES OF AROMATIC MONOCARBOXYLIC ACID.** Several representatives of the aliphatic phenyl-hydrazidines were discussed in connection with phenyl-hydrazine. The simple aromatic hydrazidines are formed when hydrazine acts on the imido-ethers. The most thoroughly investigated of these compounds is:

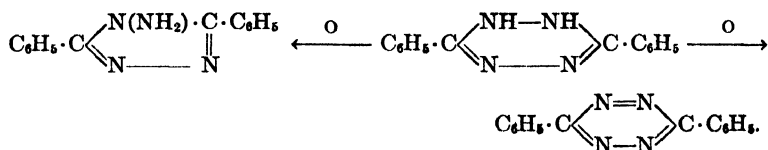
**Benzenyl-hydrazidine**,  $\text{C}_6\text{H}_5\text{C} \begin{array}{c} \text{NH}\cdot\text{NH}_2 \\ \text{NH} \end{array}$  or  $\text{C}_6\text{H}_5\text{C} \begin{array}{c} \text{N}\cdot\text{NH}_2 \\ \text{NH}_2 \end{array}$ . This compound cannot be obtained from its salts in the pure state. Its *benzoyl derivative*,  $\text{C}_6\text{H}_5\text{C}(:\text{NH})\text{NH}\cdot\text{NH}\cdot\text{COC}_6\text{H}_5$ , melts at  $188^\circ$ . It slowly loses water, even at

120°, being converted into *C*-diphenyl-triazole, and nitrous acid converts it into *diphenyl-isazoxime*, or *diphenyl-1,3,4-oxadiazole*.

The reaction between hydrazine and benzimido-ether gives rise to **dibenzoyl-hydrazidine**,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{:NH}) \cdot \text{NH} \cdot \text{NH}(\text{NH}:) \cdot \text{C} \cdot \text{C}_6\text{H}_5$  or  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NH}_2) \cdot \text{N} \cdot \text{N} \cdot (\text{NH}_2) \cdot \text{C} \cdot \text{C}_6\text{H}_5$ , m.p. 202°, and *diphenyl-dihydrotetrazine*, as well as to benzenyl-hydrazidine. Nitrous acid converts benzenyl-hydrazidine into *C*-phenyl-tetrazole.



Diphenyl-dihydrotetrazine is readily converted by acids into 1-amino-2,5-diphenyl-1,3,4-triazole. It is oxidised by the air to *diphenyl-tetrazine* (Pinner, Ber. 27, 3273; 28, 465; Ann. 297, 221; 298, 1).



**19. NITRAZONES. NITROSAZONES OR PHENYL-AZOXIMES.** These derivatives of the benzoic acids are obtained by the same methods as the corresponding aliphatic compounds (p. 162).

**Benzenyl-nitrazone**, *phenyl-nitroformaldehyde-hydrazone*,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{NO}_2 \\ \text{=NNHC}_6\text{H}_5 \end{array}$  or  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{NOOH} \\ \text{=N:NC}_6\text{H}_5 \end{array}$ , m. p. 102°, is obtained by the action of phenyldiazonium salts on phenyl-nitromethane or on nitromethane itself. It is best obtained by the action of amyl nitrite or nitrogen tetroxide on benzaldehyde-phenylhydrazone (Ciusa, Lincei, 17, I, 840). **Benzenyl-nitrosazone**,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NO}): \text{NNHC}_6\text{H}_5$ , and its more stable isomeride, **phenyl-azo-benzaldoxime**,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{NOH} \\ \text{=N:NC}_6\text{H}_5 \end{array}$ , m.p.

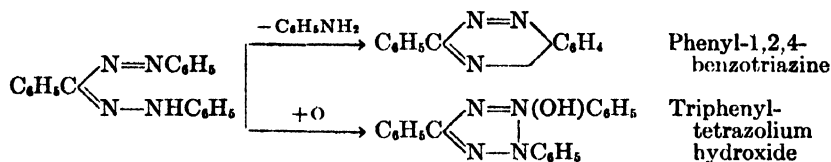
135°, are intermediate products. The latter is obtained by the action of amyl nitrite and pyridine on benzaldehyde phenylhydrazone. When phenyl-nitroformaldehyde-hydrazone is reduced by ammonium sulphide, the first product is **phenyl-hydrazo-benzaldoxime**,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NOH})\text{NHNHC}_6\text{H}_5$ , and this is oxidised by ferric chloride to phenyl-azo-benzaldoxime. The methyl ester of phenyl-nitroformaldehyde-hydrazone,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NOOCH}_3): \text{NNHC}_6\text{H}_5$ , m.p. 92°, breaks down



on boiling with alcohol into formaldehyde and phenyl-azo-benzaldoxime (*Bamberger*, Ber. 34, 2019; 36, 62, 90). *m*-Nitrobenzenyl-nitrosazone,  $\text{NO}_2\text{C}_6\text{H}_4\text{C}(\text{NO})\text{:NHC}_6\text{H}_5$ , m.p.  $98^\circ$  (decomp.), rearranges under the influence of pyridine or sodium ethylate into phenyl-azo-*m*-nitro-benzaldoxime,  $\text{NO}_2\text{C}_6\text{H}_4\text{C}(\text{NOH})\text{:N:NC}_6\text{H}_5$ , m.p.  $183^\circ$  (decomp.). The nitrosazones readily lose nitric oxide, this change taking place even when they are boiled in ether, and the residues undergo various condensations (*Bamberger*, Ber. 36, 92).

## 20. FORMAZYL DERIVATIVES OF THE AROMATIC MONOCARBOXYLIC ACIDS.\*

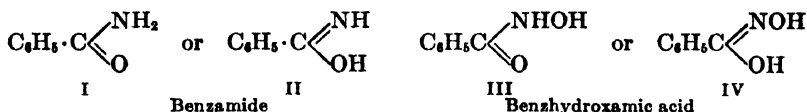
**Formazyl-benzene**,  $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{N}=\text{NC}_6\text{H}_5 \\ \text{N}-\text{NHC}_6\text{H}_5 \end{smallmatrix}$ , m.p.  $173^\circ$ , forms red leaflets, with a greenish metallic lustre. It is produced (1) by the action of diazonium salts in alkaline solution on benzaldehyde-phenylhydrazine (*Pechmann*, Ber. 27, 1690); (2) by the action of phenylhydrazine on benzenyl-amidoxime (p. 315) (*Bamberger*, Ber. 27, 160); (3) by the action of phenylhydrazine on benzophenyl-hydrazide-imidochloride. The formation of heterocyclic compounds by formazyl derivatives has already been described (p. 164). A solution of sulphuric acid in glacial acetic acid converts formazyl-benzene into phenyl-1,2,4-benzotriazine, and on oxidation formazyl-benzene gives triphenyl-tetrazolium hydroxide:



**N-Benzoyl-formazyl-benzene**,  $\text{C}_6\text{H}_5\text{C}(\text{:N:NHC}_6\text{H}_5)(\text{:N:N}[\text{COC}_6\text{H}_5]\text{C}_6\text{H}_5)$ , exists in two modifications, one forming orange-red prisms, m.p.  $146\text{--}147^\circ$ , and the other blackish-red prisms, m.p.  $139^\circ$ . It is obtained by heating benzaldehyde-diphenyl-dihydrotetrazene (p. 165) (*Busch*, Ber. 49, 2352).

**Guanazyl-benzene**,  $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{N}\cdot\text{NHC}(\text{NH}_2)\text{:NH} \\ \text{N:NC}_6\text{H}_5 \end{smallmatrix}$ , orange-yellow prisms, m.p.  $199^\circ$ , is obtained by the action of phenyl-diazonium chloride on benzalamino-guanidine, the condensation product of benzaldehyde and aminoguanidine (Vol. I, p. 515). When oxidised by nitric acid, guanazyl-benzene gives diphenyl-tetrazole (*Wedekind*, Ber. 30, 444; 31, 2353).

**21. HYDROXAMIC ACIDS, THEIR ETHERS AND ESTERS.** In connection with benzamide it was mentioned that two structural formulae were possible for this compound, the *benzamide* formula (I) and the *benzimidic acid* formula (II). If it is imagined that one of the hydrogen atoms attached to nitrogen is replaced by hydroxyl, we arrive at the two possible formulae for a hydroxamic acid:



While the amido-formula (I) is supposed to represent the carboxylic amides, the imido-ethers are derived from (II). The hydroxamic acids probably occur also in the desmotropic form (IV) (hydroximic acids). *Hydroximic chlorides* (p. 314) correspond to imidochlorides, *amidoximes* and *hydroxamoximes* to amidines, and *hydrazidoximes* to hydrazidines.

Although free benzhydroxamic acid and its homologues are known in only one form, some of their ether-like derivatives occur "in modifications of identical composition, of which the observed differences cannot be satisfactorily accounted for by differences in structure" (*Lossen*, Ann. 281, 169). *Werner* (Ber. 25, 33)

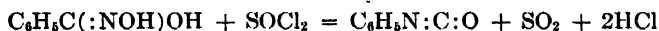
\* See page 164.

pointed out that the isomerism was due to the arrangement of the groups about the nitrogen atom, as in the oximes, the  $\alpha$ - and  $\beta$ -ethyl-benzhydroxamic acids having the following space formulae:

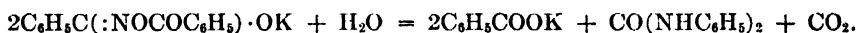


Crystallographic investigations have shown that some classes of amide-like derivatives of hydroxylamine occur in polymorphic modifications.

**Benzhydroxamic acid**,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NOH}) \cdot \text{OH}$ , m.p.  $132-133^\circ$  (*Balbiano*, *Lincei*, (5), 21, I, 389), and **dibenzhydroxamic acid**, or **benzoyl-benzhydroxamate**,  $\text{C}_6\text{H}_5\text{C}(\text{NOCOC}_6\text{H}_5)\text{OH}$ , m.p.  $161^\circ$ , are formed by the action of benzoyl action of benzoyl chloride on hydroxylamine. Benzhydroxamic acid is also formed by the oxidation of benzaldoxime with Caro's acid, by the isomerisation of phenyl-nitromethane,  $\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$ , with alkali (p. 256), and from benzaldehyde and benzene-sulphhydroxamic acid (p. 175), or nitrohydroxylaminic acid (*Bamberger*, *Ber.* 34, 2023; 35, 51; *Rimini*, *Lincei*, 10, I, 355; *Angelico*, *Gazz.* 31, II, 15; *Angeli*, *Gazz.* 33, II, 239). When silver benzoate acts upon benzo-hydroxamic chloride (p. 314), an isomer of dibenzhydroxamic acid is first formed, with m.p.  $95^\circ$ , and this readily rearranges to the higher melting isomer; some benzoic acid is also split off, and forms a certain quantity of *diphenyl-furoxan* (p. 315). A few substituted benzhydroxamic chlorides give the corresponding diphenyl-furoxans only (*Werner*, *Ber.* 32, 1654). When benzhydroxamic acid is digested with semicarbazide hydrochloride in water, benzoyl-semicarbazide (p. 303) is formed, the  $\text{NHOH}$  group being eliminated (*Rupe*, *J. pr.* 84, 809). When benzhydroxamic acid is heated with thionyl chloride in benzene solution, an intramolecular atomic migration occurs and phenyl isocyanate is formed:



(*Marquis*, *C.r.* 143, 1163). The potassium salt of dibenzohydroxamic acid is decomposed by water, especially on heating, into potassium benzoate, *sym*-*diphenyl-urea*, and carbon dioxide, phenyl isocyanate being an intermediate product:



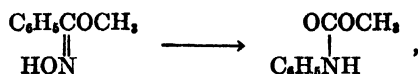
Other acyl derivatives of benzhydroxamic acid behave in a similar way. On heating with ammonia they yield *monophenyl-urea*; with alcohol, *phenyl-urethane*, i.e., transformation products of phenyl isocyanate (*Thiele*, *Ann.* 309, 189). The rearrangement occurring here recalls that of the carboxylic bromo-amides (*Hofmann*), of the acid azides (*Curtius*, p. 303), and of the ketoximes (*Beckmann*, p. 284) (*cf.* *Schroeter*, *Ber.* 42, 2336). Since it is possible to convert *sym*-*diphenyl-urea* into aniline and carbon dioxide by the action of hydrochloric acid, it is possible to use these reactions (which are capable of greater generalisation) to convert benzoic acid into aniline, i.e., to replace the  $\text{COOH}$  group by  $\text{NH}_2$  (*Lossen*, *Ann.* 175, 313).

The alkyl ethers of dibenzhydroxamic acid are known in two modifications:  $\alpha$ -(*syn*)-**methyl ether**, m.p.  $53^\circ$ ;  $\beta$ -(*anti*)-**methyl ether**, m.p.  $55^\circ$ ;  $\alpha$ -(*syn*)-**ethyl ether**, m.p.  $58^\circ$ ;  $\beta$ -(*anti*)-**ethyl ether**, m.p.  $63^\circ$  (*Gurke*, *Ann.* 205, 281; *Lossen*, *Ann.* 281, 235). The  $\alpha$ -ethers are formed by the action of alkyl iodides on the silver salt; of dibenzhydroxamic acid; the  $\beta$ -ethers are obtained by the action of benzoyl chloride and caustic potash on the alkyl-hydroxamic acids.

**Phenyl-acethydroxamic acid**,  $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{OH})\text{NOH}$ , forms thick needles or plates, m.p.  $145^\circ$ . It is prepared from ethyl phenylacetate and alcoholic hydroxylamine. Acetate, m.p.  $148-149^\circ$  benzoate, m.p.  $121^\circ$  (*Jones*, *Am. Ch. J.* 48, 1).

**ALKYL-BENZHYDROXIMIC ACIDS**, or alkyl ethers of benzhydroxamic acid,  $\text{C}_6\text{H}_5\text{C}(\text{NOH})\text{OR}$ , obtained from benzimido-ethers and hydroxylamine hydrochloride, and from dibenzhydroxamic alkyl ethers by hydrolysis (*Lossen*, *Ann.* 252, 211). They occur in two modifications, which can be distinguished by the fact that the  $\alpha$ - or *syn*-modifications give phenyl-carbamic ethers or their

transposition products when treated with phosphorus pentachloride (Beckmann transformation):



whereas the  $\beta$ - or *anti*-forms are converted into phosphoric ethers of the benzhydroxamic acids by this treatment.  $\alpha$ -(*syn*)-Methyl ether, m.p.  $64^\circ$ , readily changes to a physical isomeride, also a *syn*-modification, m.p.  $101^\circ$  (Werner, Ber. 29, 1146, 1150).  $\beta$ -(*anti*)-Methyl ether, m.p.  $44^\circ$ ;  $\alpha$ -(*syn*)-ethyl ether, m.p.  $53^\circ$ ;  $\beta$ -(*anti*)-ethyl ether, m.p.  $68^\circ$ . The alkyl-benzhydroxamic acids also form alkyl and acyl ethers.

**Tribenzoyl-hydroxylamine**,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{:NOCOC}_6\text{H}_5)\text{OCOC}_6\text{H}_5$ , is obtained in three forms by the action of benzoyl chloride on hydroxylamine hydrochloride;  $\alpha$ - m.p.  $100^\circ$ ;  $\beta$ - m.p.  $141^\circ$ ;  $\gamma$ - m.p.  $112^\circ$ . The  $\alpha$ - and  $\gamma$ -forms are converted into the  $\beta$ -form by the action of hydrochloric acid (Lossen, Ann. 281, 276).

**Thiobenzhydroxamic acid**,  $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{SH} \\ \diagup \\ \text{NOH} \end{smallmatrix}$ , an unstable oil, is formed by the ac-

tion of hydroxylamine on dithiobenzoic acid. The dibenzoyl-compound melts at  $92^\circ$  (Cambi, Lincei 18, I, 687).

**22. HALIDES OF BENZHYDROXIMIC ACIDS.** The free chlorides, and ethers of fluorides, chlorides, and bromides, are known. The free chlorides have been prepared from the corresponding benzaldoximes by the action of chlorine in chloroform solution, or of nitrosyl chloride (Rheinboldt, Ann. 451, 161). Their ethers are obtained by treating amidoxime ethers with hydrogen halides and alkali nitrite, or with excess nitrosyl chloride, and by the action of phosphorus pentachloride on alkyl hydroxamates. The hydroximic chlorides react as follows: with ammonia they give *amine-oximes*; with hydroxylamine, *hydroxam-oximes*; with aniline, toluidine, etc., *anilides*. On standing, and more rapidly on heating, they decompose with formation of *azoxime oxides* and nitriles. With sodium carbonate they lose HCl and give nitrile oxides (see below). For their reactions with silver salts, see p. 313 (Werner, Ber. 32, 1975).

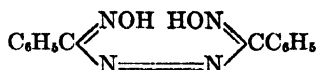
**Benzhydroximic chloride**,  $\text{C}_6\text{H}_5\text{C}(\text{:NOH})\text{Cl}$ , m.p.  $49^\circ$ , is obtained from benzaldoxime, and gives *N-hydroxy-C-diphenyl-tetrazole*,  $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{N(OH) \cdot N} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{N} \end{smallmatrix}$ , with sodium azide (Forster, J. 95, 184). **Benzenyl-methoxime chloride**,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{:NOCH}_3)\text{Cl}$ , b.p.  $225^\circ$ . **Benzenyl-ethoxime bromide**,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{:NOC}_2\text{H}_5)\text{Br}$ , b.p.  $239^\circ$  (Tiemann, Ber. 24, 3454).

**Benzenyl-hydroxylamine-acetic acid**,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{:NOCH}_2\text{COOH})\cdot\text{OH}$ , m.p.  $135\text{--}138^\circ$ , is formed when caustic potash acts upon **benzenyl-nitroxime-acetic acid**,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{:NOCH}_2\text{COOH})\text{ONO}$ , m.p.  $95^\circ$ , the product of the action of sulphuric acid and potassium nitrite on benzenyl-aminoxime-acetic acid (see below). **Benzenyl-fluoro-, chloro-, and bromo-oxime-acetic acid**, all melting at  $135^\circ$ , are obtained by the action of the hydrogen halides and potassium nitrite on benzenyl-aminoxime-acetic acid (Werner, Ber. 26, 1570).

**23. BENZONITROLIC ACID**,  $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{NOH} \\ \diagup \\ \text{NO}_2 \end{smallmatrix}$ , light yellow needles, with a very bitter taste, m.p.  $58^\circ$  (decomp.), is formed by the action of nitrous acid on phenyl-*aci*-nitromethane (p. 256), and in small yield by the oxidation of benzonitrosolic acid (see below) with permanganate (Wieand, Ber. 39, 2522). It is much more unstable than the paraffin-nitrolic acids, and readily decomposes on standing, and instantly on heating, into nitrous acid and *diphenyl-furozan*, with intermediate formation of *benzo-nitrile oxide*. It gives an orange coloration with alkalis. The solution of the alkali salts decomposes spontaneously into alkali nitrite and tribenzo-nitrile oxide.

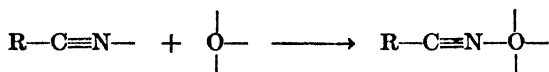
**24. BENZONITROSOLIC ACID**,  $\text{C}_6\text{H}_5\cdot\text{C} \begin{smallmatrix} \text{NOH} \\ \diagup \\ \text{NO} \end{smallmatrix}$ , is obtained in the form

of its dark blue salts by the action of aqueous alkalis, or ammonia, on benzhydroxyamoxime; the very unstable red azo-compound,



is formed intermediately, and is split up by hydrolysis into benzenylamidoxime and benzo-nitrosolic acid. The free acid is unstable; when liberated from its salts it decomposes into nitrous acid and benzonitrile. When the silver salt (pink needles, decomp. at 94°) is acted upon by iodine, *diphenyl-furozan* is formed (Wieland, Ber. 39, 1480).

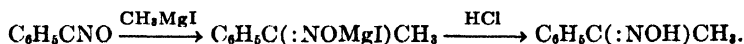
25. **NITRILE OXIDES.** Nitrile oxides contain the group  $\text{—C} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ , or, more probably,  $\text{—C}\equiv\text{NO}$ , the oxygen being attached to the carbon of the nitrile group as shown by the electronic formulae:



A dash represents a two-electron bond. This formulation shows that it is possible to regard the nitrile oxides as the anhydrides of hydroxamic acids, to which, in fact, they are closely related by their method of formation. **Benzonitrile oxide**,  $\text{C}_6\text{H}_5\text{C}=\text{NO}$ , forms a mobile oil, with a penetrating odour, resembling that of a nitrile. It solidifies to a crystalline mass when strongly cooled, and melts at 15°. It is obtained by removing hydrogen chloride from benzhydroximic chloride by means of sodium carbonate solution. On keeping, it quickly polymerises to

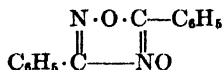
*diphenyl-furozan*,  $\text{C}_6\text{H}_5\cdot\text{C} \begin{array}{c} \text{N} \quad \text{O} \\ \parallel \quad \parallel \\ \text{N} \cdot \text{O} \cdot \text{NO} \end{array} \cdot\text{C}\cdot\text{C}_6\text{H}_5$  (Wieland, Ber. 40, 1667; 42, 4207). On

heating in xylene solution, it partly isomerises to phenyl isocyanate. It is decomposed by concentrated hydrochloric acid to benzoic acid and hydroxylamine, while zinc dust and glacial acetic acid reduce it to benzonitrile. It combines with methylmagnesium iodide to form acetophenone oxime:



(Cf. Beckmann transformation, p. 284.)

A trimeric form of benzonitrile oxide is formed by the spontaneous decomposition of an aqueous solution of sodium benzo-nitrolate, sodium nitrite being eliminated. **Tribenzo-nitrile oxide**,  $(\text{C}_6\text{H}_5\text{CNO})_3$ , decomposes at 130° with explosion when rapidly heated. In its reactions it resembles the monomeric compound. When heated in toluene solution it depolymerises, with formation of phenyl isocyanate. With aniline it yields diphenyl-urea, and when reduced it gives benzonitrile. Alcoholic hydrochloric acid decomposes it partly into *diphenyl-1,2,4-oxadiazole*;

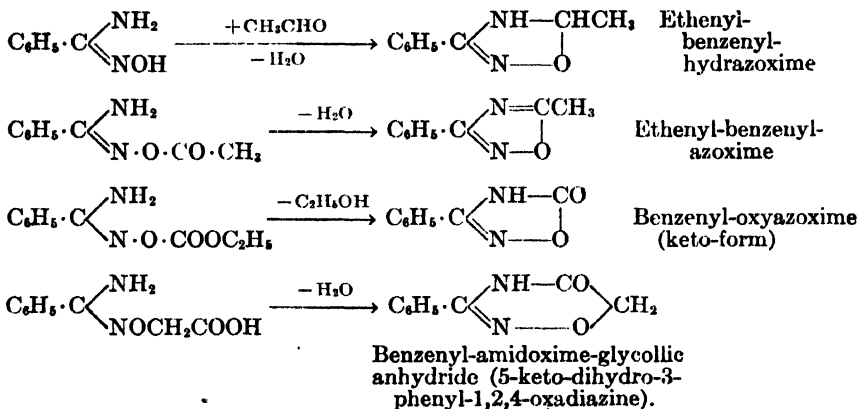


26. **AMIDE OXIMES** are obtained by the action of hydroxylamine on thioamides (p. 308), nitriles (p. 305), imido-ethers (p. 308), and amidines (p. 309); and from hydroximic chloride by the action of ammonia. Their alcoholic solutions give a deep-red colour with ferric chloride.

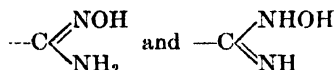
**Benzenyl-amidoxime**, benzhydroxamic amide,  $\text{C}_6\text{H}_5\text{C}(:\text{NOH})\text{NH}_2$ , m.p. 79°, gives the carbylamine reaction with chloroform and caustic potash. It is converted into benzamide by nitrous acid. It forms salts with both acids and caustic alkalis, such as  $\text{C}_6\text{H}_5\cdot\text{C}(:\text{NOH})\cdot\text{NH}_2\text{HCl}$  and  $\text{C}_6\text{H}_5\cdot\text{C}(\cdot\text{NH}_2):\text{NOK}$ . The latter yields ethers with alkyl iodides. Methyl ether,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{NH}_2):\text{NOCH}_3$ , m.p. 57°, ethyl ether, m.p. 67° (Lossen, Ann. 281, 280).

**Acetyl-benzenyl-amidoxime**,  $C_6H_5 \cdot C(:NHC(=O)CH_3) \cdot NH_2$ , m.p.  $16^\circ$  (*Schule*, Ber. 18, 1082). **Benzenyl-oximido-carbonic ester**,  $C_6H_5C(:NH_2):NOC(=O)OC_2H_5$ , m.p.  $127^\circ$ . **Benzenyl-oximido-glycollic acid**,  $C_6H_5C(:NH_2):NO \cdot CH_2COOH$ , m.p.  $123^\circ$ . **Benzenyl-amidoxime butyric acid**,  $C_6H_5C(NH_2):NOCH(C_2H_5)COOH$ , m.p.  $82^\circ$  (*Werner*, Ber. 29, 2655).

**Formation of heterocyclic compounds from amidoximes.**—The amidoximes condense with aliphatic aldehydes giving *hydrazoximes*. The amidoxime acid derivatives, referred to above, when heated above their m.p. lose water or alcohol, forming *azoximes*.



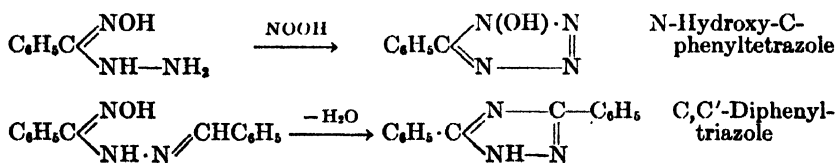
The amidoximes and the hydroxy-amidines are tautomeric:



Hydroxy-amidines are formed from imidochlorides by the action of  $\beta$ -aryl-hydroxylamines (*Ley*, Ber. 34, 2620; 36, 18). **Benzenyl-phenyl-*p*-tolyl-hydroxy-amidine**,  $C_6H_5C(NC_6H_5)N(C_6H_7)OH$ , m.p.  $175^\circ$ , and **benzenyl-*p*-tolyl-phenyl-hydroxy-amidine**,  $C_6H_5C(NC_6H_7)N(C_6H_5)OH$ , m.p.  $191^\circ$ , form the same phenyl-tolyl-benzamidine when reduced with sulphurous acid.

**27. HYDRAZIDOXIMES** are produced by the action of hydrazine hydrate on benzhydroximic chloride in alcoholic solution. Like the amidoximes, they are amphoteric, dissolving in acids as well as in alkalis. The latter readily decompose them, nitrogen being liberated.

**Benzenyl-hydrazidoxime**,  $C_6H_5 \cdot C \begin{array}{l} \nearrow NOH \\ \searrow NHNH_2 \end{array}$ , m.p.  $110^\circ$  (decomp.), gives N-hydroxy-C-phenyl-tetrazole with nitrous acid. It condenses with benzaldehyde to **benzal-benzenyl-hydrazidoxime**,  $C_6H_5C(:NOH)NH \cdot N:CHC_6H_5$ , m.p.  $120^\circ$ . The latter readily hydrazidises with acids to C,C'-diphenyl-triazole (*Wieland*, Ber. 42, 4199):



**28. HYDROXAMOZIMES** (p. 260). **Benzhydroxamoxime**,  $C_6H_5C(NOH) \cdot NHOH$ , m.p.  $115^\circ$  (decomp.), is formed by the action of hydroxylamine on benzhydroximic chloride. It gives a reddish-brown copper salt,  $(C_7H_7N_2O_2)_2Cu$

(*Ley*, Ber. 31, 2126). Alkalis convert it into a red azo-compound, which is further hydrolysed to benzenyl-amidoxime, and salts of benzo-nitrosolic acid (*Wieland*, Ber. 39, 1480).

#### DERIVATIVES OF ORTHOBENZOIC ACID

29. **ETHYL ORTHOBENZOATE**,  $C_6H_5C(OC_2H_5)_2$ , b.p.  $238^\circ$ , is obtained from phenyl-chloroform and sodium ethoxide, or by the action of ethyl ortho-carbonate on phenyl-magnesium bromide (*Tshitshababin*, Ber. 38, 564).

30. **BENZOTRICHLORIDE**, *phenyl-chloroform*,  $C_6H_5 \cdot CCl_3$ , m.p.  $-22.5^\circ$  (*Haase*, Ber. 26, 1053), b.p.  $213^\circ$ , sp. gr. 1.38, isomeric with the chloro-benzal chlorides, dichloro-benzyl chlorides, and the trichlorotoluenes. Benzotrichloride bears the same relationship to benzoic acid as methyl-chloroform does to acetic acid. It is formed (1) by passing chlorine into boiling toluene until there is no further increase in weight (*Beulstein*, Ann. 146, 330); (2) by the action of phosphorus pentachloride on benzyl chloride (*Limpricht*, Ann. 139, 326). When heated to  $100^\circ$  with water it is converted into benzoic acid. When digested with anhydrous oxalic acid it gives benzoyl chloride and benzoic anhydride (*Anschütz*, Ann. 226, 20). It reacts with organic sulphonates with formation of sulphonyl chlorides and benzoyl chloride, or benzoates (Fr. Pat. 739,290). It readily condenses with anilines or phenols to form triphenyl-methane derivatives (*Döbner*, Ber. 15, 232; *Orndorff*, Am. 49, 818, 992).

**Benzo-trifluoride**,  $C_6H_5CF_3$ , b.p.  $103^\circ$ , is formed, together with difluoro-chloro-toluene,  $C_6H_5CClF_2$ , b.p.  $143^\circ$ , by the action of antimony trifluoride on benzotrichloride (*Swarts*, Bull. Belg. 1898). For chlorinated and nitrated benzotrichlorides, see Ger. Pats. 229,873 and 234,290; *Spreckels*, Ber. 52, 315; *Sah*, Tsing-Hua Rep. 1933. For halogenated benzo-trifluorides, see *Booth*, Am. 57, 2064, 2066.

**Orthobenzoic acid piperide**,  $C_6H_5C(N \cdot C_6H_{10})_3$ , m.p.  $80^\circ$ , is formed by warming benzo-trichloride with piperidine.

The benzamide-halides (p. 306) also belong to the derivatives of *o*-benzoic acid.

#### Substituted Aromatic Monocarboxylic Acids

Only those monocarboxylic acids will here be dealt with which are derived from benzene by substitution of nuclear hydrogen atoms. Certain ortho-compounds have the power of forming internal anhydrides or heterocyclic compounds, with elimination of water.

See p. 296 for the behaviour of 2,6-substituted carboxylic acids when esterified with alcohol and hydrochloric acid.

##### 1. HALOGEN-SUBSTITUTED BENZOIC ACIDS are formed:

1. By substitution of benzoic acids or nitriles. The first halogen atom to enter takes the *m*-position with respect to carboxyl (p. 14) (*Varma*, Indian, 7, 503). 2. By oxidising *p*- and *m*-halogen-substituted toluenes and higher homologues with chromic acid, and *o*-halogen-substituted hydrocarbons with dilute nitric acid, or potassium permanganate. In the animal organism, halogen-substituted toluenes are converted into the corresponding halogen-substituted hippuric acids (p. 301) (*Hildebrandt*, C. 1903, I, 411). 3. From the amino-acids (*a*) by converting them into the diazonium sulphates, or (*b*) by converting them into diazo-amino acids. When both classes of substances are boiled with halogen acids, the corresponding halogen-carboxylic acid is formed. Fluoro-benzoic acids have been prepared in this way from diazoamino-acids (*Paterno*, Gazz. 1882, 85).

4. By the action of phosphorus pentachloride on hydroxy-acids (see salicylic acid). 5. *Nuclear synthesis*: by heating the halogen-nitro-benzenes with

potassium cyanide and alcohol to 200–230°. The cyanide group takes the place of the nitro-group; it does not, however, take the same place in the benzene residue (*Richter*, Ber. 8, 1418; *Lobry de Bruyn*, Rec. 23, 47). At the temperature of the reaction, the nitrile is converted into the acid. *m*-Chloro-nitrobenzene gives *o*-chlorobenzoic acid, and *p*-chloro-nitrobenzene gives *m*-chlorobenzoic acid. 6. From the halogen-substituted anilines, *via* the diazonium compounds, *etc.*

**Properties and reactions.**—The melting points of the ortho-halogen-substituted benzoic acids are the lowest of the three, and those of the para-acids are the highest, as the table below shows. The melting point rises with increasing atomic weight of the substituting halogen. The ortho-derivatives are fairly soluble in water, and form readily soluble barium salts, which permits their easy separation from *m*- and *p*-derivatives. They do not readily react with magnesium, even though it be activated (*Salkind*, C. 1915, I, 833). With ammonia and amines, and copper, *o*-chlorobenzoic acid forms anthranilic and *N*-alkyl-anthranilic acids (p. 325) (*Ullmann*, Ann. 355, 312). Sodium-*o*-chlorobenzoate, or a mixture of *o*- and *p*-chlorobenzoates is used as a preservative under the name of "Microbin." The melting points follow:

|                          | ortho- | meta- | para- |
|--------------------------|--------|-------|-------|
| Fluorobenzoic acid. .... | 126.5° | 124°  | 182°  |
| Chlorobenzoic acid. .... | 140°   | 157°  | 240°  |
| Bromobenzoic acid. ....  | 147°   | 156°  | 254°  |
| Iodobenzoic acid. ....   | 162°   | 187°  | 267°  |

The separation of *o*- and *p*-halogenobenzoic acids has been carried out making use of the principle of fractional neutralisation with alkalis, the ortho-acid having the highest dissociation constant, and therefore being the strongest acid, reacting with the greater amount of alkali (U. S. Pat. 1,942,826).

Many polychloro-, polybromo-, and polyiodo-benzoic acids are known. All five hydrogen atoms of benzoic acid can be replaced by chlorine or bromine. *o*-Chlorobenzoyl chloride, m.p. 93–95° (10 mm.), is prepared by the action of chlorine on *o*-chlorobenzaldehyde at 140–160° (*Clarke*, Org. Synth. 9, 34).

**2. IODOSO- AND IODOXY-BENZOIC ACIDS** (p. 52). The three iodo-benzoic acids, when chlorinated in chloroform solution, give iodochloro-benzoic acids, and when these are treated with sodium hydroxide they give iodoso-benzoic acids (*Willgerodt*, Ber. 27, 2326). *o*-Iodoso-benzoic acid,  $C_6H_4(IO)COOH$ , forms leaflets with a satin lustre, melting above 200° (decomp.). It is also obtained from *o*-iodobenzoic acid by oxidation with fuming nitric acid (*Meyer*, Ber. 28, 83), and from *o*-iodotoluene (*Montagne*, Weekbl. 13, 1294) by oxidation with potassium permanganate. *o*-Iodoxy-benzoic acid,  $C_6H_4(IO_2)COOH$ , is a by-product in the last-mentioned reaction; it melts at

233°, with violent explosion. The formula  $C_6H_4 \begin{matrix} I(OH) \\ \diagup \quad \diagdown \\ CO \end{matrix}$  has also been suggested for *o*-iodoso-benzoic acid, as it yields an acetyl derivative when heated with acetic anhydride, in the same way as laevulinic acid does; **acetiiodoso-benzoic acid**,

$C_6H_4 \begin{matrix} I(OCOCH_3) \\ \diagup \quad \diagdown \\ CO \end{matrix}$ , m.p. 166° (*Askenasy*, Ber. 26, 1364).

**3. NITRO-SUBSTITUTED MONOCARBOXYLIC ACIDS.** Not more than three nitro-groups have been introduced into the benzene residue of an aromatic carboxylic acid.

**NITROBENZOIC ACIDS.** (1) Meta-nitrobenzoic acid is the principal product when benzoic acid is nitrated; the *o*- and *p*-compounds are also formed, but in much smaller quantity (*Widemann*, Ann. 193, 202; *Hollemann*, Z. physik. Ch. 31, 79).

(2) Nitrobenzoic acids have been obtained by oxidising the nitrotoluenes: *o*-nitrotoluene is oxidised with potassium permanganate (*Monnet*, Ber. 12, 443), or with nitric acid vapour at about 140° (Russ. Pats. 9,324 and 10,952); *m*- and *p*-nitrotoluene are oxidised with chromic acid mixture (*Beilstein*, Ann. 155, 25); and *p*-nitrotoluene has been oxidised electrolytically (*Dunnbrook*, Trans. Am. Electroch. Soc. 45). *o*- and *p*-Nitrobenzoic acids are also produced by oxidising

*o*- and *p*-nitrobenzyl chloride with potassium permanganate (Noelting, Ber. 17, 385), and by oxidising *o*- and *p*-nitrocinnamic acids.

(3) The nitrobenzoic acids are also prepared by converting the three isomeric nitranilines into the three nitrobenzonitriles. The nitration of benzonitrile gives *m*-nitrobenzonitrile almost exclusively. *o*-Nitrobenzonitrile has been obtained from *o*-nitraniline (Pinner, Ber. 28, 150). The nitro-acids are obtained, of course, by hydrolysing the nitro-nitriles with caustic soda. The melting points follow:

*o*-Nitrobenzoic acid, 148°  
*m*-Nitrobenzoic acid, 142°  
*p*-Nitrobenzoic acid, 240°

*o*-Nitrobenzonitrile, 110°  
*m*-Nitrobenzonitrile, 118°  
*p*-Nitrobenzonitrile, 149°

*o*-Nitrobenzoic acid has a sweet taste, and dissolves in 164 parts of water at 16°. When nitrated it gives 2,6-, 2,5-, and 2,4-dinitrobenzoic acids, and styphnic acid (p. 223). *o*-Nitrobenzoyl chloride, m.p. 25° (Mavrojoannis, C.r. 132, 1054). *m*-Nitrobenzoic acid dissolves in 425 parts of water (16°). Its barium salt is difficultly soluble. When nitrated it gives 2,5-dinitrobenzoic acid. *p*-Nitrobenzoic acid (chloride, m.p. 75°; anhydride, m.p. 190°; see Thiele, Ann. 314, 305) is very sparingly soluble in water. When nitrated it gives 2,4- and 3,4-dinitrobenzoic acids. The electrolysis of its warm solution in sulphuric acid gives *p*-*aminophenol sulphonic acid* (Noyes, Am. Ch. J. 16, 511; Ger. Pat. 77,806). 2,4-, 3,4-Dinitro-, and 2,4,6-trinitro-benzoic acids are obtained by the oxidation of the corresponding nitrotoluenes (p. 63). The dinitrotoluenes are oxidised by chromic acid mixture (Haussermann, Ber. 27, 2209), or by potassium permanganate. Trinitrotoluene is oxidised by a nitric acid-sulphuric acid mixture at 150-220°.

*o*-Nitrobenzhydrazide, m.p. 120°, obtained from *o*-nitrobenzoic acid and hydrazine hydrate, is a reagent for aldehydes and ketones (Sah, Rep. Tsing. Hua 3, 461).

Dinitrobenzoic acids, 2,3- m.p. 204°; 2,4- m.p. 183°; 2,5- m.p. 179°; 2,6- m.p. 206°; 3,4- m.p. 165°; 3,5-(ordinary) m.p. 205°. 2,4,6-Trinitrobenzoic acid, (NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>COOH, obtained by oxidation of 2,4,6-trinitrotoluene, melts at 210°, with loss of carbon dioxide (Meyer, Ber. 27, 3154; Grell, Ber. 28, 2564; Jackson, Ber. 28, 3065; Ger. Pat. 77,559; Clarke, Org. Synth. 1, 528). It also loses carbon dioxide when boiled with water (Secareanu, Bull. 53, 1395). The following trinitrobenzoic acids are obtained by oxidising the corresponding trinitrotoluenes with nitric acid or chromic-sulphuric acid: 2,3,4- m.p. 222-223°; 2,4,5- m.p. 190-191°; 2,3,6- m.p. 160° (Giua, Lincei, 23, II, 484; Korner, Lincei, 25, II, 339). Chlorimido-*m*-nitrobenzoic methyl ester,

NO<sub>2</sub>[3]C<sub>6</sub>H<sub>3</sub>C $\begin{smallmatrix} \swarrow \text{NCl} \\ \searrow \text{OCH}_3 \end{smallmatrix}$ , is formed by the action of diazomethane on benzoyl-chlor-

amide (p. 300); it occurs in two stereoisomeric forms, m.p. 88° and 84°; gaseous hydrogen chloride reduces both to the same *m*-nitro-benzimido-methyl ether, NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>C(:NH)OCH<sub>3</sub>, and when the latter is acted upon by sodium hypochlorite, a mixture of the two isomers is re-formed (Hilpert, Am. 40, 156).

**NITRO-HALOGENO-BENZOIC ACIDS** (Holleman, Rec. 20, 235; Purgotti, Gazz. 32, I, 526). *o,o*-Fluoro-nitrobenzoic acid, C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)FCOOH, m.p. 139°, obtained by oxidation of *o*-fluoro-nitrotoluene, or by action of nitric acid on *o*-fluorobenzoic acid (Gonert, Rec. 33, 325). In contrast with the other *o,o*-disubstituted benzoic acids, it can be quite readily esterified (van Loon, Ber. 29, 842). 4,6-Mononitro-chlorobenzoic acid, m.p. 165°, and two dinitro-chlorobenzoic acids, m.p. 238° and 200°, are formed by nitrating *o*-chlorobenzoic acid (Ger. Pat. 106,510). The nitration of *m*-bromobenzoic acid gives two *o*-nitro-acids, both of which yield anthranilic acid on reduction. These acids are 3-bromo-2-nitrobenzoic acid, m.p. 250°, and 3-bromo-6-nitrobenzoic acid, m.p. 139° (compare the equivalence of the six hydrogen atoms of benzene, p. 8). The halogen atom in the nitro-halogen-benzoic acids is reactive, as in the case of the nitro-halogeno-benzenes (Schopff, Ber. 22, 3282).

**NITRO-PHENYLACETIC ACIDS**, NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>COOH, are obtained by hydrolysing the nitro-benzyl cyanides with caustic alkali. These cyanides are obtained by acting on the nitro-benzyl chlorides with potassium cyanide (Gabriel,



## 320 SUBSTITUTED AROMATIC MONOCARBOXYLIC ACIDS

Ber. 16, 2064; *Bamberger*, Ber. 19, 2635). When phenylacetic acid is nitrated the product is chiefly the *p*-nitro-compound; but a little of the *o*-compound is formed together with some *o,p*-dinitro-phenylacetic acid, m. p. 166°. The latter can also be obtained from 2,4-dinitro-phenyl-acetoacetic ester by hydrolysis with dilute sulphuric acid (*Borsche*, Ber. 42, 2276). Their nitriles in ether solution form dark-brown or violet salts with sodium ethoxide. These are presumably derivatives of the *aci*-form (*Opolski*, Ber. 49, 2276).

*o*-, *m*-, *p*-Nitrophenylacetic acid, m.p. 141°, 120°, 152°, resp.  
*o*-, *m*-, *p*-Nitrobenzyl cyanide, m.p. 84°, 61°, 116°, resp.

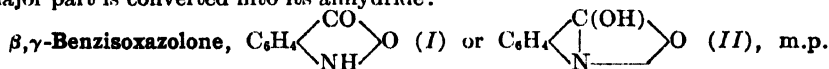
**NITROHYDROCINNAMIC ACIDS**,  $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ . *p*-Nitro- and *o*-nitro-hydrocinnamic acids are produced by the nitration of hydrocinnamic acid. Both give the *o,p*-dinitro-acid when further nitrated. The *o*-nitro-acid is also prepared from *o*-nitro-*p*-amino-hydrocinnamic acid, the primary reduction product of the *o,p*-dinitro-acid, and from *o*-nitro-benzyl-malonic ester. The *m*-nitro-acid is obtained from *p*-acetoamino-*m*-nitro-hydrocinnamic acid (*Gabriel*, Ber. 15, 846; *Reissert*, Ber. 29, 635; cf. also *m*-nitrotoluene, p. 64).

*o*-, *m*-, *p*-Nitrohydrocinnamic acid, m.p. 115°, 118°, 163°, resp.  
*o,p*-Dinitrohydrocinnamic acid, m.p. 123° (*Gabriel*, Ber. 12, 600).

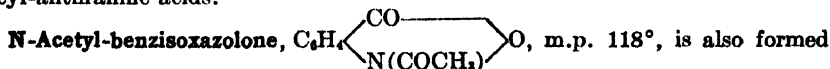
*o*- and *p*-Nitrohydratropic acids,  $\text{NO}_2\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\cdot\text{COOH}$ , m.p. 110° and 87°, respectively, are formed by adding hydratropic acid to strongly cooled fuming nitric acid (*Trimus*, Ann. 227, 262).

**4. NITROSO-MONOCARBOXYIC ACIDS.** *o*-Nitrosobenzoic acid,  $\text{C}_6\text{H}_4\text{[2]NO[1]COOH}$  m.p. 210° (decomp.), forms colourless crystals, which give a green solution. It is obtained by oxidation of anthranilic acid with Caro's acid (*Bamberger*, Ber. 36, 3651), and by photochemical change of *o*-nitrobenzaldehyde in indifferent solvents. It is also formed by the action of ammonium cyanide on *o*-nitrobenzaldehyde (*Heller*, J. pr. 106, 1). In alcoholic solutions the following esters are produced: *methyl ester*, m.p. 157°; *ethyl ester*, m.p. 121° (*Bamberger*, Ann. 371, 319). When *o*-nitro-benzylidene-aniline,  $\text{C}_6\text{H}_4\text{[1]NO}_2\text{[2]CH:NC}_6\text{H}_5$ , is exposed to light it gives *o*-nitrosobenzanilide,  $\text{C}_6\text{H}_4(\text{NO})\text{CONHC}_6\text{H}_5$  (*Sachs*, Ber. 35, 2715; 36, 4373). Connected with these methods of formation is that of *o*-nitrosobenzoic acid by the action of ammonia on *o*-nitromandelic nitrile,  $\text{NO}_2\text{[1]C}_6\text{H}_4\text{[2]CH(OH)CN}$ , when hydrocyanic acid is eliminated (*Heller*, Ber. 39, 2335). *o*-Nitrosobenzoic acid is also formed when phenyl-hydroxy-indole is oxidised. 4-Nitro- and 2,4-dinitro-*o*-nitrosobenzoic acid are transformation products of 2,4-dinitro-, and 2,4,6-trinitro-benzaldehyde when exposed to light (p. 277). *o*-, *m*-, and *p*-Nitrosobenzoic acids and their esters, are also obtained by the oxidation of the corresponding hydroxylamino-benzoic acids, which are themselves formed by reduction of nitrobenzoic acids (*Alway*, Ber. 37, 333).

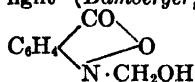
**5. HYDROXYLAMINO-CARBOXYLIC ACIDS.** *o*-Hydroxylamino-benzoic acid,  $\text{C}_6\text{H}_4\text{[2]NHOH[1]COOH}$ , m.p. 142° (decomp.) forms brilliant needles. It is obtained by reducing *o*-nitrobenzoic acid with zinc dust and ammonium chloride. It has the general properties of hydroxylamine-compounds. It is oxidised to *o*-nitroso-benzoic acid, with which it condenses in alkaline solution to *o,o'*-azoxybenzoic acid. On warming with dilute sulphuric acid, it is partly converted into 5-hydroxy-anthranilic acid,  $\text{OH[5]C}_6\text{H}_3\text{[2]NH}_2\text{[1]COOH}$ , while the major part is converted into its anhydride:



112° (decomp.). This substance is an acid. The alkali salts must be regarded as derived from the hydroxy-anthranil formula (II) because of their very difficult decomposition to salts of *o*-hydroxylamino-benzoic acid. The alkyl- and acyl-benzisoxazolones derived from these alkali salts, however, must be regarded as derived from formula I, since on reduction they readily form N-alkyl- and N-acyl-anthranilic acids.



by condensation of *o*-nitrosobenzoic acid with paraldehyde under the influence of light (*Bamberger*, Ber. 42, 2297). **N-Methylol-benzisoxazolone**,

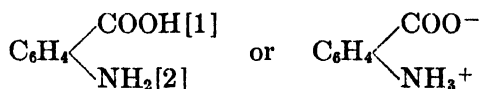


, m.p. 117°, is obtained from benzisoxazolone and formaldehyde, or by the rearrangement of *o*-nitroso-benzoyl-carbinol (p. 405). When heated with acids it gives *methylene-bis-benzisoxazolone*, m.p. 162° (decomp.). It follows that this compound will be produced when acids act upon *o*-nitroso-benzoyl carbinol or *o*-nitrophenyl-ethylene oxide (p. 400) (*Arndt*, Ber. 60, 454).

### 6. Aromatic Amino-carboxylic Acids

Aromatic amino-carboxylic acids are obtained from the nitro-monocarboxylic acids by reduction. Like glycocoll, they form salts with alkalis as well as with mineral acids, but not with acetic acid. Hence they are precipitated from their alkali salts by the addition of acetic acid. Like glycocoll, too, these acids may be regarded as cyclic ammonium salts (Vol. I, p. 440). The hydrogen atoms of the amino-group can be replaced by alkyl or acyl groups. Dimethyl-amino acids can also be obtained from dimethyl-anilines by the action of carbonyl chloride and aluminium chloride. Acetamino-benzoic acids are prepared by oxidising acet-toluidides. The ortho-amino-acids readily form heterocyclic compounds, and give some interesting ortho-condensation products. Thus, *o*-aminobenzoic acid and *o*-amino-phenylacetic acids are closely related to indigo, and *o*-aminohydrocinnamic acid to quinoline.

**Anthranilic acid**, *o*-aminobenzoic acid, m.p. 145°,



sublimes at low pressures substantially without decomposition (*Scheuermann*, Chem. Ztg. 27, 245), but breaks down into aniline and CO<sub>2</sub> when heated under ordinary pressures. Its aqueous solution has a sweet taste. Its solutions, especially those in certain organic solvents, show a blue fluorescence (*Pawlewski*, Ber. 31, 1693). Anthranilic acid was discovered by *Fritzsche* (1841), who obtained it from indigo by the action of potash. The oxidation can be accelerated by the addition of manganese dioxide (*Hand*, Ann. 234, 146). It has also been obtained: by reducing *o*-nitrobenzoic acid or either of the two *m*-bromo-*o*-nitrobenzoic acids (p. 319) with tin and hydrochloric acid, or electrolytically (*Rao*, Current Sci. 3, 552); by heating nitrotoluene (p. 63) with concentrated caustic potash (*Preuss*, Z. Angew. Ch. 1900, 385; *Scholl*, Mo. 34, 1011); from anthranil, or acetoanthranilic acid, or isatoic anhydride; or from isatin by the action of peroxides in alkaline solution (Ger. Pat. 375,616) (*cf.* *o*-chlorobenzoic acid). It is manufactured industrially by treating phthalimide, C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NH, with bromine and alkali (*Hoogewerff*, Rec. 10, 4; *Tscherniac*, Ber. 36, 218; *Mohr*, J. pr. 80, 1): C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NK + KOBr + 2KOH = C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)COOK + KBr + K<sub>2</sub>CO<sub>3</sub>; by the action of sodium hypochlorite on phthalamic acid (*Chapman*, J. 127, 1791),

or by the action of alkali on phthalyl-hydroxylamine,  $C_6H_4(CO)_2NOH$  or  $C_6H_4(COOH)C(OH)NOH$  (Ger. Pat. 136,788).

Nitrous acid acts on aqueous solutions of anthranilic acid, converting the acid into salicylic acid. An amyl alcohol solution of the acid is reduced by sodium to hexahydro-anthranilic acid, hexahydro-benzoic acid, and *n*-pimelic acid (Vol. I, p. 561) (*Einhorn*, Ber. 27, 2466). The lead and silver salts of anthranilic acid react with thionyl chloride, giving *N*-thionyl-anthranilic chloride,  $COCl \cdot C_6H_4 \cdot NSO$ , in brilliant yellow needles, m.p. 34–35° (*Anschütz*, Ber. 62, 826). For the action of phosphorus pentachloride on anthranilic acid, see below.

**Methyl anthranilate**, m.p. 25.5°, b.p. 125° (9 mm.), is a characteristic constituent of orange-blossom or neroli oil, and is also found in the oil from the flowers of *Tuberosa* (*Walbaum*, Ber. 32, 1512; *Hesse*, Ber. 36, 1465); its solution has a strong blue fluorescence. **Ethyl anthranilate**, b.p. 260°. These esters can be obtained directly from phthalimide by the action of alkali hypochlorite on its alcoholic-alkaline solutions (Ger. Pat. 139,218), or from isatoic anhydride by the action of sodium ethoxide and water (*Bredt*, Ber. 33, 28). The amide, m.p. 108°, was prepared by *Kolbe* in 1885 (J. pr. 30, 467), by the action of ammonia on isatoic anhydride. *as*-Phenylhydrazide, m.p. 134° (*Roesler*, Ann. 301, 89).

**Anthranilic nitrile**, *o*-amino-benzonitrile,  $NH_2[2]C_6H_4CN$ , m.p. 49°, b.p. 267°, is obtained by the action of stannous chloride and hydrochloric acid on *o*-nitro-benzonitrile (*Reissert*, Ber. 42, 3711), or by removal of water from *o*-amino-benzaldoxime (*Gabriel*, Ber. 36, 804). When heated with ammonium sulphide, it gives the thioamide,  $NH_2C_6H_4CSNH_2$ , m.p. 122°, and with nitrous acid it forms a diazo-compound, which is reduced by stannous chloride to  $\gamma$ -amino-indazole (*Bogert*, Am. 25, 372; *Reissert*, Ber. 42, 3716).

The chloride of anthranilic acid is itself not known, but its hydrochloride has been prepared. **Anthranoyl-chloride hydrochloride**,  $ClOC[1]C_6H_4[2]MH_2 \cdot HCl$ , is formed by the action of hydrochloric acid on an ether solution of *o*-thionyl-amino-benzoyl chloride,  $ClOC \cdot [1]C_6H_4[2]N:S:O$ . From anthranoyl chloride hydrochloride and acetylene-dimagnesium bromide, **di-anthranoyl-acetylene**,  $H_2N[2]C_6H_4[1]CO \cdot C:C \cdot CO[1]C_6H_4[2] \cdot NH_2$ , m.p. 161–162° (decomp.) has been obtained (*Anschütz*, Ber. 62, 826; Ann. 493, 241). With phosphorus pentachloride, anthranilic acid gives the compounds  $ClOC \cdot C_6H_4 \cdot NH \cdot POCl_2$ , m.p. 62°, and  $[(ClOC \cdot C_6H_4NH)_2PO]_2N \cdot C_6H_4COCl$ , m.p. 148–153° (*Uhlfelder*, Ber. 36, 1824).

**Anthranilino-sodium-methylene sulfoxylate**,  $COOH \cdot C_6H_4NH \cdot CH_2OSONa + 2H_2O$ , m.p. 96°, obtained from anthranilic acid and sodium formaldehyde-sulphoxylate, gives **N-sulphethyl-anthranilic acid**,  $COOH \cdot C_6H_4 \cdot NH \cdot S \cdot C_2H_5$ , m.p. 97–99°, when treated with ethyl-mercaptan (*Binz*, Ber. 53, 2017).

**Formyl-anthranilic acid**,  $CHONH[2]C_6H_4COOH$ , m.p. 169°, is obtained by boiling isatoic anhydride with formic acid, by the action of formic acid on anthranilic acid, by the action of chromium trioxide on formyl-isatin (*Hantzsch*, Ber. 57, 195), and by the action of chloroform and caustic potash on anthranilic acid (*Passerini*, Gazz. 58, 636). On heating, it condenses to 4-keto-dihydro-

quinazoline-2-benzoic acid,  $C_6H_4 \begin{matrix} \diagup CO \cdot NC_6H_4COOH \\ | \\ N=CH \end{matrix}$  (*Anschütz*, Ber. 35, 3475).

**Acetoanthranilic acid**,  $CH_3CONHC_6H_4COOH$ , m.p. 186°, is produced when anthranilic acid is treated with acetic anhydride; by the oxidation of acet-*o*-toluidide with potassium permanganate in the presence of magnesium sulphate (*Ullmann*, Ber. 36, 1801); and by the oxidation of methyl-ketol and of quinaldine. The methyl ester m.p. 61°, and the amide, m.p. 170°, have been obtained from methyl anthranilate and anthranilamide, respectively. When acetoanthranilic acid, or its ester, is heated with phosphorus oxychloride, the so-called *dianhydro-diaceto-anthranilic acid*,  $C_{18}H_{14}N_2O_4$ , m.p. 250°, is formed. When heated with acetic anhydride to 150°, or by itself to 200–210°, acetoanthranilic acid is partly anhydridised to acetoanthranil, and partly condensed to methyl-dihydro-quinazo-

lone-benzoic acid,  $C_6H_4 \begin{matrix} \swarrow \text{CO} \cdot \text{NC}_6\text{H}_4\text{COOH} \\ \searrow \text{N}=\text{CCH}_3 \end{matrix}$  (Anschütz, Ber. 35, 3470).

**Benzoyl-anthranilic acid**,  $C_6H_5\text{CONHC}_6\text{H}_4\text{COOH}$ , m.p.  $183^\circ$ , see *Bamberger*, Ber. 26, 1304; *Heller*, Ann. 324, 134. **N-Acetonil-anthranilic acid**,  $\text{COOH} \cdot C_6H_4 \cdot \text{NH} \cdot \text{CH}_2\text{COCH}_3$ , m.p.  $169-170^\circ$ , has been prepared from anthranilic acid by the action of chloroacetone in aqueous potassium carbonate (*Houben*, Ber. 43, 3533). **Benzene-sulphone anthranilic acid**,  $C_6H_5\text{SO}_2\text{NHC}_6\text{H}_4\text{COOH}$ , m.p.  $214^\circ$  chloride, m.p.  $155^\circ$  (*Schroeter*, Ann. 367, 104).

**Anthranil**,  $C_6H_4 \begin{matrix} \swarrow \text{CH} \\ \searrow \text{NO} \end{matrix}$ , see p. 278.

**Acetoanthranil**,  $C_6H_4 \begin{matrix} \swarrow \text{CO} \cdot \text{O} \\ \searrow \text{N}=\text{CCH}_3 \end{matrix}$  or  $C_6H_4 \begin{matrix} \swarrow \text{CO} \\ \searrow \text{NCOCH}_3 \end{matrix}$ , m.p.  $81^\circ$ ,

b.p.  $147^\circ$  (14 mm.), can be obtained from anthranil or acetoanthranilic acid, or carbethoxy-anthranilic acid, by the action of acetic anhydride. It must therefore be regarded as a true anhydride of acetoanthranilic acid. With ammonia it gives *o*-acetamino-benzamide, and with aniline and other amines it gives deriva-

tives of *methyl-dihydro-quinazolin*,  $C_6H_4 \begin{matrix} \swarrow \text{CO} \cdot \text{NR} \\ \searrow \text{N}-\text{C} \cdot \text{CH}_3 \end{matrix}$ . **Benzoyl-anthranil**

$C_6H_4 \begin{matrix} \swarrow \text{CO} \cdot \text{O} \\ \searrow \text{N}=\text{C} \cdot C_6H_5 \end{matrix}$  or  $C_6H_4 \begin{matrix} \swarrow \text{CO} \\ \searrow \text{NCOC}_6H_5 \end{matrix}$ , m.p.  $122^\circ$ , behaves similarly. It is ob-

tained from benzoyl-anthranilic acid by removal of water; from anthranilic acid, benzoyl chloride, and pyridine in the cold; and by heating anthranil for several hours with benzoyl chloride (*Anschütz*, Ber. 35, 3480; *Heller*, Ber. 36, 2766). The ready formation of acyl-anthranils from the acyl-anthranilic acids, and the close relationship existing between these compounds and the quinazolones point to the first formula for acetoanthranil, rather than the second. This is supported by the anhydride formation of those acyl-anthranilic acids, such as benzene-sulphone-anthranilic acid, and picryl-anthranilic acid, in which the forma-

tion of compounds of the formula  $C_6H_4 \begin{matrix} \swarrow \text{CO} \cdot \text{O} \\ \searrow \text{N}=\text{CR} \end{matrix}$  is impossible. In these cases

dimolecular anhydrides are formed instead of  $\beta$ -lactams,  $C_6H_4 \begin{matrix} \swarrow \text{CO} \\ \searrow \text{NCOR} \end{matrix}$ ; cf.

di-anthranilides (below), and *Schroeter*, Ann. 367, 124. The acyl-anthranils must therefore be regarded as  $\alpha, \beta$ -benzomeloxazines and are closely related to the anhydrides obtained from benzoyl- $\alpha$ -amino-acids, such as hippuric acid, benzoyl-alanine, etc. (p. 302).

**Dimolecular anhydrides of anthranilic acid** (*Schroeter*, Ann. 367, 101). Dimolecular anhydrides are known of anthranilic acid: anthranoyl-anthranilic acid, anthranoyl-anthranilic anhydride (anthranoyl-anthranil), and dianthranilide; all these can be decomposed to anthranilic acid.

**Anthranoyl-anthranilic acid**,  $\text{NH}_2[2]C_6H_4[1] \text{CONH}[2]C_6H_4[1] \text{COOH}$ , m.p.  $203^\circ$ , is formed: (1) by reduction of *o*-nitro-benzoyl-anthranilic acid; (2) by condensation of anthranilic acid with isatoic anhydride and hence (3) as an intermediate product in the industrial preparation of anthranilic acid from phthalimide, sodium hypochlorite and sodium hydroxide (*Mohr*, J. pr. 80, 1). When heated above its melting point, or, more readily, by the action of thionyl chloride, water eliminated, and **anthranoyl-anthranilic-O-anhydride**, **anthranoyl-anthranil**

$C_6H_4 \begin{matrix} \swarrow \text{CO} \cdot \text{O} \\ \searrow \text{N}=\text{CC}_6H_4\text{NH}_2 \end{matrix}$ , m.p.  $162^\circ$ , is formed as yellow needles, which readily polymerise on heating. Its *benzene-sulphone compound*,

$C_6H_4 \begin{matrix} \swarrow \text{CO} \cdot \text{O} \\ \searrow \text{N}=\text{CC}_6H_4\text{NH} \cdot \text{SO}_2\text{C}_6H_5 \end{matrix}$ , m.p.  $273^\circ$ , is formed by the action of benzene sulphonyl chloride on anthranil (*Mohr*, Ber. 40, 997). By repeatedly treating anthranoyl-anthranilic acid with nitro-benzoyl chloride, and then reducing the

product, anhydrides of anthranilic acid are obtained which resemble the polypeptides in nature, e.g.,  $\text{NH}_2\text{C}_6\text{H}_4\text{CO}\cdot\text{NHC}_6\text{H}_4\text{CO}\cdot\text{NHC}_6\text{H}_4\text{COOH}$ , etc. (Meyer, Ann. 351, 267).

**Dianthranilide**,  $\text{C}_6\text{H}_4\begin{matrix} \text{NH}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{NH} \end{matrix}\text{C}_6\text{H}_4$ , m.p. about  $330^\circ$ , colourless needles, is obtained from its monoacetyl-compound, which is itself prepared by the action of concentrated sulphuric acid and glacial acetic acid on dibenzene-sulphone-dianthranilide, by boiling with sodium hydroxide. It is a weak dibasic acid, and gives a disodium salt, which, on methylation with dimethyl sulphate, gives N,N-

**dimethyl-dianthranilide**,  $\text{C}_6\text{H}_4\begin{matrix} \text{N}(\text{CH}_3)\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}\cdot(\text{CH}_3)\text{N} \end{matrix}\text{C}_6\text{H}_4$ . Dianthranilide is broken down into two molecules of anthranilic acid by boiling with concentrated alkali.

**Dibenzene-sulphone-dianthranilide**,  $\text{C}_6\text{H}_4\begin{matrix} \text{N}(\text{SO}_2\text{C}_6\text{H}_5)\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}(\text{C}_6\text{H}_5\text{SO}_2)\text{N} \end{matrix}\text{C}_6\text{H}_4$ , m.p.  $264^\circ$ , is formed by heating benzene-sulphone-anthranilic chloride with pyridine.

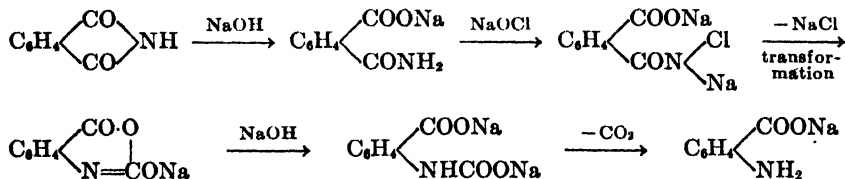
**Carboxyl-anthranilic dimethyl ester** and **diethyl ester**,  $\text{C}_6\text{H}_4(\text{NHCOOCH}_3)_2$ , m.p.  $61^\circ$ , b.p.  $166^\circ$  (12 mm.), and m.p.  $44^\circ$ , b.p.  $174^\circ$  (10 mm.), are obtained by the action of sodium alkoxides on phthalimide chloride or bromide,  $\text{C}_6\text{H}_4(\text{CO})_2\text{NBr}$ ; further action converts them into the *hydrogen isatoic esters*: **N-carbomethoxy- and N-carboethoxy-anthranilic acids**,  $\text{C}_6\text{H}_4(\text{NHCO}_2\text{Alk})\text{COOH}$ , m.p.  $181^\circ$  and  $126^\circ$ , also obtained from anthranilic acid by the action of chloroformic esters, and from isatoic anhydride by heating it with alcohols. Treatment with acetyl chloride converts them into:

**Isatoic anhydride**,  $\text{C}_6\text{H}_4\begin{matrix} \text{CO}\cdot\text{O} \\ | \\ \text{NH}\quad\text{CO} \end{matrix}$ , m.p. about  $240^\circ$  (decomp.). This substance

was first obtained by oxidising a solution of indigo in glacial acetic acid with chromic acid (Kolbe, 1885), and later from anthranil and anthranilic acid by the action of chlorocarbonic esters (Niementowski, Ber. 22, 1672). It has also been obtained by passing carbonyl chloride into sodium anthranilate solution. It is very difficultly soluble in water. With alkalis or alkaline earths, it forms

unstable salts of the formula  $\text{C}_6\text{H}_4\begin{matrix} \text{CO}\cdot\text{O} \\ | \\ \text{N}=\text{COMe} \end{matrix}$  from which carbon dioxide re-

generates isatoic anhydride. With excess of alkali, salts of isatoic acid are first formed, but these, when digested with alkali, or instantly on adding acids, are broken up into carbon dioxide and anthranilic acid. Free isatoic acid cannot therefore be obtained (Erdmann, Ber. 32, 2159; Bredt, Ber. 33, 21; Mohr, J. pr. 79, 281). Ammonia, hydrazine, phenylhydrazine, and hydroxylamine convert it into the corresponding derivatives of anthranilic acid (Meyer, J. pr. 33, 18; Finger, J. pr. 48, 92). Isatoic anhydride is an intermediate product in the manufacture of anthranilic acid from phthalimide, sodium hypochlorite, and sodium hydroxide, and can be isolated if excess of sodium hydroxide is avoided. The processes involved are represented in the following formulae (Mohr, J. pr. 80, 1):



**Kynuric acid**, *oxalyl-anthranilic acid*,  $\text{COOH}\cdot\text{CONH}[2]\text{C}_6\text{H}_4[1]\text{COOH} + \text{H}_2\text{O}$ , m.p. (anhydrous)  $180^\circ$  (decomp.) is an oxidation product of quinoline derivatives, such as *kynurine*, *kynurenic acid*,  $\alpha$ -phenyl-quinoline, *carbostyryl* (p. 468), and *aceto-tetrahydro-quinoline*, and of *indoxyl acid*. It is also formed by a rearrangement of N-hydroxy-dihydro-indole, taking place at ordinary temperature (Heller, Ber. 55, 480). It has been synthesised by heating anthranilic and oxalic acids

at 130° (*Schiff*, *Ber.* 17, 401; *Kretschy*, *Mo.* 5, 16). Its *monoethyl ester*,  $\text{COOC}_2\text{H}_5\text{CONH}[2]\text{C}_6\text{H}_4[1]\text{COOH}$ , m.p. 180°, is an oxidation product of indoxyl ester (*Baeyer*, *Ber.* 15, 778).

**Oxalyl-anthranilic-nitrile acid**, *o*-cyanoxanilic acid,  $\text{COOH}\cdot\text{CONH}[2]\text{C}_6\text{H}_4[1]\text{CN}$ , m.p. 126°. Its methyl ester, m.p. 139°, has been obtained by condensing *o*-amino-benzonitrile with methyl oxalate. Under the influence of dilute acids, oxalyl-anthranilic-nitrile acid rearranges to 4-*keto-dihydroquinazoline-2-*

*carboxylic acid*,  $\text{C}_6\text{H}_4\begin{matrix} \swarrow \text{CO}\cdot\text{NH} \\ \searrow \text{N}=\text{C}\text{COOH} \end{matrix}$  (*Reissert*, *Ber.* 42, 3710). The same tendency to heterocyclic ring closure, and formation of quinazolone compounds is observed when anthranilic acid is treated with cyanogen. In water the reactants combine to form the nitrile of the last-named acid, 2-**cyano-3,4-dihydro-quin-**

**azolone**,  $\text{C}_6\text{H}_4\begin{matrix} \swarrow [1]\text{CO}\cdot\text{NH} \\ \searrow [2]\text{N}=\text{C}\cdot\text{CN} \end{matrix}$ , which decomposes on melting. In alcohol, 2-**ethoxy-1,4-dihydro-4-quinazolone**,  $\text{C}_6\text{H}_4\begin{matrix} \swarrow \text{CO}\cdot\text{N} \\ \searrow \text{NHC}\cdot\text{OC}_2\text{H}_5 \end{matrix}$ , m.p. 173° is formed (*Griess*, *Ber.* 2, 415). The latter is converted by ammonia into 2-**amino-1,4-**

**dihydro-4-quinazolone**,  $\text{C}_6\text{H}_4\begin{matrix} \swarrow [1]\text{CO}\cdot\text{N} \\ \searrow [2]\text{NH}\cdot\text{CNH}_2 \end{matrix}$ , and when this is heated with methyl iodide in strongly alkaline solution,  $\alpha$ -*o*-benzo-creatinine,

$\text{C}_6\text{H}_4\begin{matrix} \swarrow [1]\text{CO}\text{---}\text{N} \\ \searrow [2]\text{N}(\text{CH}_3)\text{---}\text{C}\cdot\text{NH}_2 \end{matrix}$ , is formed (*Griess*, *Ber.* 11, 1986; 13, 977).

**Methyl-anthranilic acid**,  $\text{CH}_3\text{NH}[2]\text{C}_6\text{H}_4[1]\text{COOH}$ , m.p. 182°, is obtained by the action of methyl iodide and sodium carbonate on anthranilic acid, or by the action of dimethyl sulphate on anthranilic acid in methyl alcoholic, or aqueous solution. It is also formed by the action of methylamine and copper on *o*-chlorobenzoic acid (*Ger. Pat.* 145,604). The methyl ester,  $\text{CH}_3\text{NHC}_6\text{H}_4\text{COOCH}_3$ , m.p. 18°, b.p. 129° (13 mm.), occurs in the oil from the leaves and skins of mandarin oranges (*Citrus nobilis*) (*Charabot*, *C.r.* 135, 580). When heated with sod-

amide, or alkali- or alkaline-earth-amalgams, the acid is converted into *indoxyl* and *indigo*, and its N-acyl derivatives enter into this reaction even more readily.

**Formylmethyl-anthranilic acid**,  $\text{CHON}(\text{CH}_3)\text{C}_6\text{H}_4\text{COOH}$ , m.p. 169°, and **formylethyl-anthranilic acid**, m.p. 119°, can be prepared by oxidising methyl- and ethyl-quinolinium salts with permanganates (*Ullmann*, *Ber.* 36, 1806; *Ger. Pat.* 139,393). **N-Nitrosomethyl-anthranilic acid**,  $\text{NO}\cdot\text{N}(\text{CH}_3)\text{C}_6\text{H}_4\text{COOH}$ , m.p. 127°, is obtained by the action of nitrous acid on methyl-anthranilic acid, or by oxidising nitrosomethyl-*o*-toluidine with potassium permanganate (*Vorländer*, *Ber.* 34, 1644). Under the influence of hydrogen chloride it polymerises to 5-**nitrosomethyl-anthranilic acid**,  $\text{NO}[5]\text{C}_6\text{H}_3[2]\text{NHCH}_3[1]\text{COOH}$ , and this, when boiled with sodium carbonate solution, loses methylamine and gives 5-nitrososalicylic acid (p. 361). When the aqueous solution of its potassium salt is heated with acetic anhydride it gives an intense blood-red compound, soluble in water (*Houben*, *Ber.* 42, 2745; 43, 3533). On further methylation, methyl-anthranilic acid gives **dimethyl-anthranilic acid**,  $(\text{CH}_3)_2\text{N}[2]\text{C}_6\text{H}_4[1]\text{COOH}$ , m.p. 70°, and

**anthranilic betaine**, *o*-benzo-betaine,  $\text{C}_6\text{H}_4\begin{matrix} \swarrow \text{N}(\text{CH}_3)_3^+ \\ \searrow \text{COO}^- \end{matrix}$ , m.p. 227°. At 240°, the latter rearranges to **methyl dimethyl-anthranilate**, b.p. 121° (11 mm.) (*Willstätter*, *Ber.* 37, 411). See also *m*- and *p*-aminobenzoic acids (p. 328), and anilidoacetic acid (p. 90), and betaine (Vol. I, p. 442). **Ethyl-anthranilic acid**, m.p. 153° (*Houben*, *Ber.* 39, 3236). **Diethyl-anthranilic acid**, m.p. 121° (*Meyer*, *Mo.* 25, 487).

Aryl-anthranilic acids are formed by heating *o*-chlorobenzoic acid with aromatic amines, in the presence of copper (*Ullmann*, *Ann.* 355, 312). When heated alone they split off carbon dioxide, and give diphenylamines (p. 84), and when heated with concentrated sulphuric acid, they give acridones. **Phenyl-anthranilic acid**,  $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{COOH}$ , m.p. 181°, is also obtained by deaminating anilido-

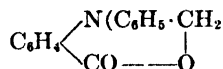
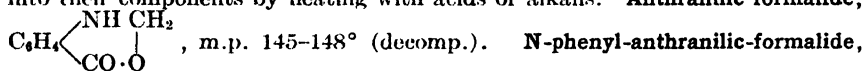
phenyl-anthranilic acid. **Diphenyl-anthranilic acid**,  $(\text{C}_6\text{H}_5)_2\text{NC}_6\text{H}_4\text{COOH}$ , m.p.

208°, is obtained by the action of iodobenzene on phenyl-anthranilic acid, in the presence of copper. When heated, it decomposes into carbon dioxide and triphenylamine (Goldberg, Ber. 40, 2448). **Picryl-anthranilic acid**,  $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{NHC}_6\text{H}_4\text{COOH}$ , m.p. 272° (Schroeter, Ann. 367, 118). **Diphenylamine-*o,o'*-*o,m'*-** and ***o,p'*-dicarboxylic acids**,  $\text{CO}_2\text{HC}_6\text{H}_4\text{NHC}_6\text{H}_4\text{COOH}$ , m.p. 295°, 296°, and 290° (decomp.), respectively, are obtained from *o*-chlorobenzoic acid and *o*-, *m*-, and *p*-aminobenzoic acid, respectively (Ullmann, Ann. 355, 352). ***sym*-Diphenyl-*p*-phenylene-diamine-*o,o'*-dicarboxylic acid**, *sym-p*-phenylene-diamine-bis-*o*-benzene-carboxylic acid,  $\text{COOH}[1]\text{C}_6\text{H}_4[2]\text{NH}[1]\text{C}_6\text{H}_4[4]\text{NH}[2]\text{C}_6\text{H}_4[1]\text{CO}_2\text{H}$ , m.p. 288° (decomp.), is obtained from *p*-dibromobenzene and anthranilic acid, in the presence of copper (Ger. Pat. 173,523).

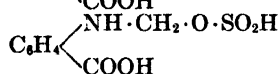
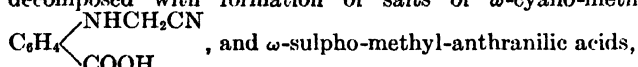
Formaldehyde condenses with anthranilic acid in various molecular proportions, according to the conditions.

**Methylene-dianthranilic acid**, *formaldehyde-dianthranilic acid*,  $\text{CH}_2(\text{NH}[2]\text{C}_6\text{H}_4\text{COOH})_2$ , m.p. 158° (decomp.), is formed from 2 mols. of anthranilic acid and 1 mol. of formaldehyde. Methyl-alcoholic hydrogen chloride converts it into *p*-**2-diamino-diphenyl-methane-dicarboxylic acid**,  $\text{CH}_2[\text{C}_6\text{H}_4(\text{NH}_2)\text{COOH}]_2$  (p. 84); by acetylation with acetic anhydride and sodium acetate, *methylene-diace-to-anthranilic acid*,  $\text{CH}_2[\text{N}(\text{COCH}_3)\text{C}_6\text{H}_4\text{COOH}]_2$ , is formed. Potassium cyanide splits formaldehyde-dianthranilic acid into anthranilic acid and anthranilido-acetonitrile (Heller, Ann. 324, 118).

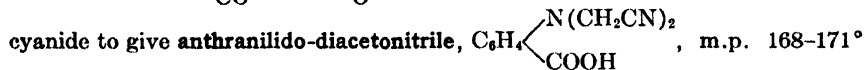
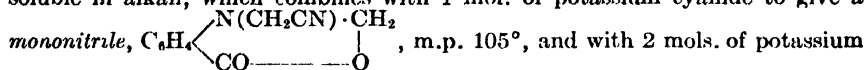
By condensation of equimolecular proportions of formaldehyde and anthranilic acid, and its *N*-mono-substitution products,  $\text{CO}_2\text{HC}_6\text{H}_4\text{NHR}$ , the **formalides** are obtained. These substances are *insoluble in alkalis*, and may be used for characterising, and isolating, substituted anthranilic acids, as they are readily resolved into their components by heating with acids or alkalis. **Anthranilic formalide**,



When treated with potassium cyanide, or alkali bisulphite, the formalides are decomposed with formation of salts of  $\omega$ -cyano-methyl-anthranilic acids,



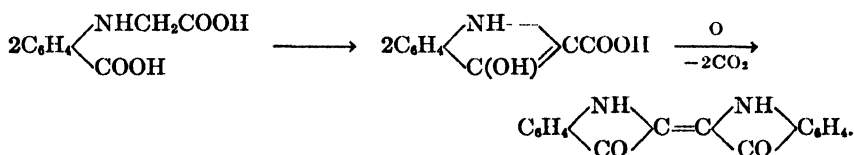
Anthranilic acid combines with excess of formaldehyde on heating to form **anthranilic diformalide**. This is a heavy yellow oil, insoluble in alkali, which combines with 1 mol. of potassium cyanide to give a



(decomp.) (Villiger, Ber. 42, 3534; Ger. Pat. 216,749). **Methylene-anthranilic acid**,  $\text{COOH}\text{C}_6\text{H}_4\text{N}:\text{CH}_2$ , m.p. about 210° (Houben, Ber. 41, 1565).

**Phenyl-glycine-*o*-carboxylic acid**, *anthranilido-acetic acid*,  $\text{COOH}[2]\text{C}_6\text{H}_4\text{NHCH}_2\text{COOH}$ , m.p. 215° (decomp.), has become of great technical importance because of its transformation into *indoxyl* and *indigo*. It is formed: (1) from chloroacetic and anthranilic acids, in neutral solution; with excess of chloroacetic acid, **anthranilido-diacetic acid**,  $\text{COOH}\text{C}_6\text{H}_4\text{N}(\text{CH}_2\text{COOH})_2$ , m.p. 212° (decomp.), is obtained (Vorländer, Ber. 33, 3182); (2) by heating anthranilic acid with polyhydric alcohols, such as glycerol, mannitol, etc. (Ger. Pat. 111,067); (3) by hydrolysis of anthranilido-acetonitrile,  $\text{COOH}[2]\text{C}_6\text{H}_4\text{NHCH}_2\text{CN}$ , m.p. 181° (decomp.) which is obtained from anthranilic acid, formaldehyde, and potassium cyanide, or by decomposing formaldehyde-anthranilic acid, or anthranilic formalide with potassium cyanide (Heller, Ann. 324, 114; Kohner, J. pr. 63, 392; Bu-

cherer, Ber. 39, 989); (4) from *o*-chlorobenzoic acid by heating with glycooll in the presence of alkaline carbonates and copper (Ger. Pats. 172,507 and 143,902). When heated with caustic alkalis, or acetic anhydride and sodium acetate, the acid is converted into *indoxyl* and its derivatives, which are in turn readily converted into *indigo*:

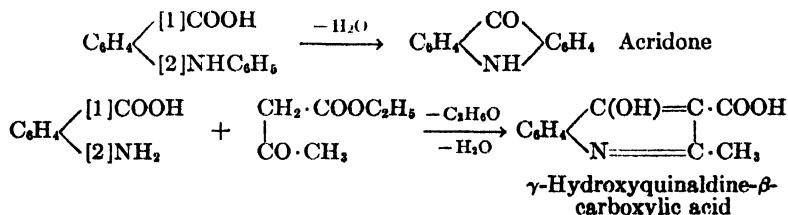


The esters: **dimethyl ester**, m.p. 97°; **diethyl ester**, m.p. 75°, condense to *indoxyl* esters under the influence of sodium ethoxide. The condensation of anthranilido-acetic acid, and its esters, is facilitated by acyl or alkyl groups attached to the nitrogen atom: *aceto-anthranilido-acetic acid*,  $\text{COOHC}_6\text{H}_4\text{N}(\text{COCH}_3)\text{CH}_2\text{COOH}$ , m.p. 214° (decomp.); **diethyl ester**, m.p. 64°. *Methyl-anthranilido-acetic acid*,  $\text{COOHC}_6\text{H}_4\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$ , m.p. 189° (decomp.) (Vorländer, Ber. 35, 1683). *Phenyl-anthranilido-acetic acid*,  $\text{COOHC}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)\text{CH}_2\text{COOH}$ , m.p. 166°. The nitrile of this acid is obtained by the action of potassium cyanide on anthranilic-formaldehyde (Ger. Pat. 216,749).

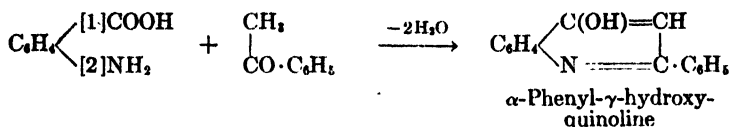
***p*-Sulpho-anthranilic acid**,  $\text{SO}_3\text{H}[4]\text{NH}_2[2]\text{C}_6\text{H}_3\text{COOH}$ , is obtained from *o*-nitro-toluene-sulphonic acid and sodium hydroxide, a method similar to the formation of anthranilic acid from *o*-nitrotoluene (p. 321; Ger. Pat. 138,207). For *o*-thionyl-aminobenzoyl chloride, see p. 322. **3,5-Dibromo-anthranilic acid**, m.p. 232°, is obtained from *o*-nitrotoluene (Friedlander, Mo. 28, 987), or anthranilic acid by the action of bromine (Elion, Rec. 42, 145). Five of the six possible **dichloro-anthranilic acids** are known (Villiger, Ber. 42, 3533, 3549; Ger. Pats. 216,749 and 220,839). **Tetrachloro-anthranilic acid**,  $\text{Cl}_4\text{C}_6[2]\text{NH}_2[1]\text{COOH}$ , m.p. 182°, is obtained from tetrachloro-phthalic anhydride (Villiger, loc. cit.), **5-Nitro-anthranilic acid**,  $\text{NO}_2[5]\text{NH}_2[2]\text{C}_6\text{H}_3\text{COOH}$ , m.p. 269°, is obtained by various methods, for example, through its aceto-compound, m.p. 221°, which is itself obtained by oxidation of nitro-aceto-toluidide with calcium permanganate (Ullmann, Ber. 36, 1801), and together with the isomeric acid,  $\text{NO}_2[4]\text{NH}_2[2]\text{C}_6\text{H}_3\text{COOH}$ , by the action of potassium hypobromite on 4-nitro-phthalimide (Seidel, Mo. 23, 415). Similarly, 3- and 6-nitro-anthranilic acids, m.p. 203° and 180° (decomp.), are formed by the action of potassium hypobromite on 3-nitro-phthalimide (Kahn, Ber. 35, 472, 3863). **Dinitro-anthranilic acid**,  $(\text{NO}_2)_2[3,5]\text{NH}_2[2]\text{C}_6\text{H}_3\text{COOH}$ , m.p. 265°, is obtained by the action of ammonia on dinitro-chlorobenzoic acid. **5-Nitroso-N-alkyl-anthranilic acids**, see Houben, Ber. 53, 2352.

**Formation of heterocyclic compounds by anthranilic acid and its derivatives.**—It is evident from that fact that anthranilic acid forms acyl-anthranils, isatoic anhydride, and indoxyl, and other substances mentioned above, that the acid and its derivatives readily form heterocyclic systems by "ortho-" condensation [cf. *o*-amino-benzyl-alcohol (p. 262); *o*-amino-benzaldehyde (p. 279); and *o*-amino-acetophenone (p. 286)].

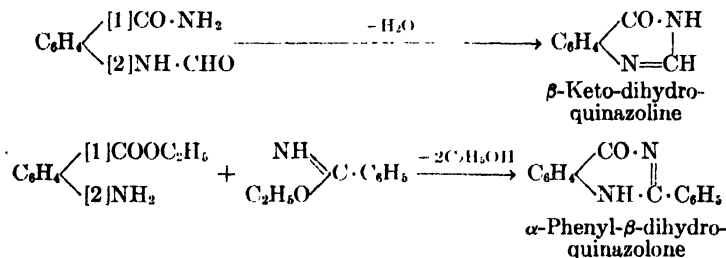
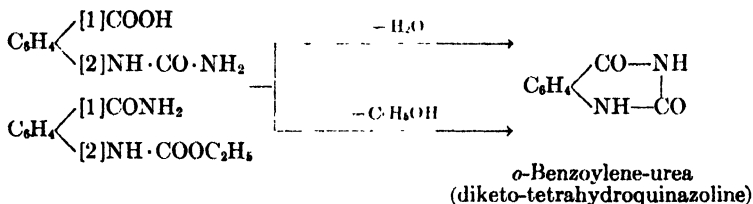
Acetyl-anthranilic acid and phenol condense on heating to *acridone*, which is also formed when phenyl-anthranilic acid is digested with concentrated sulphuric acid (Schopf, Ber. 25, 2740). Anthranilic acid condenses with acetophenone and acetoacetic ester to give derivatives of *quinoline* (Niementowski, Ber. 27, 1396).



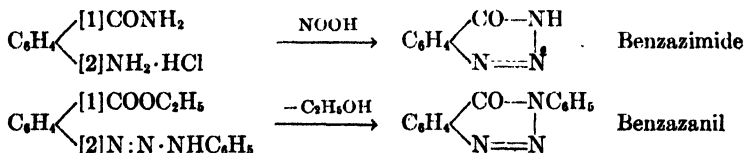




*o*-Benzoylene-urea, is formed when anthranilic acid, or anthranilamide is heated with urea, and by heating *N*-carbethoxy-*o*-aminobenzamide (Griess, 1869; Abt, J. pr. 39, 148). It is also formed by the action of mineral acids on uramido-benzoic acid (Paal, Ber. 27, 976). Derivatives of *keto-dihydroquinazoline* are formed on heating formyl-, acetyl-, and benzoyl-*o*-aminobenzamides. The 2-methyl compound is obtained by the action of acetamide on anthranilic acid, by the action of ammonia on ethyl-acetamino-benzoate, and by the action of acetic anhydride on anthranilo-nitrile (Weddige, J. pr. 36, 141; Abt, J. pr. 39, 140; Niementowski, Ber. 27, R 516; Bogert, Am. 24, 1031; 25, 372).  $\alpha$ -Phenyl- $\beta$ -keto-dihydroquinazoline is formed when ethyl anthranilate is heated with benzimino-ethyl ester (Finger, J. pr. 74, 154). The condensation products of anthranilic acid and cyanogen have been mentioned above.



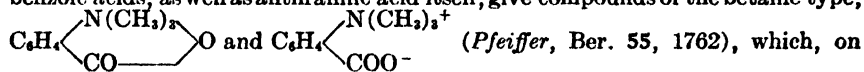
Anthranilamide reacts with nitrous acid with the direct formation of *benzazimide*; ethyl anthranilate gives the same product indirectly, *o*-diazobenzoic ester,  $\text{C}_6\text{H}_4(\text{COOC}_2\text{H}_5)\text{N}_2\text{Cl}$ , being first formed, and then acted upon by the ammonia. Similarly, anthranil-thioamide (p. 322), gives *thiobenzazimide* (Reisert, Ber. 42, 3719). *o*-Diazaminobenzene-carboxylic ester, m.p. 76°, gives *benzazanyl* (1-*keto*-2-phenyl-dihydro-1,2,3-benzotriazine), when boiled with alcohol (Finger, J. pr. 37, 431; Mehner, J. pr. 64, 70).



*m*- and *p*-AMINO BENZOIC ACIDS, m.p. 173° and 186°, respectively; methyl esters, m.p. 36–38° and 112°; ethyl esters, b.p. 294°, and m.p. 91–92°, respectively. The aceto-compounds of the free acids, m.p. 248° and 250°, are produced by oxidising *m*- and *p*-acetotoluidide with permanganates (Ullmann, Ber. 36, 1801). A number of derivatives of *p*-aminobenzoic acid are used as anaes-

thetics; the ethyl ester is known as *anaesthesin*, and the isobutyl ester as *cycloform*. For condensation products of anaesthesin with acyl chlorides, see C. 1931, I, 1276. *p*-Aminobenzonitrile, m.p. 86°, *m*-aminobenzonitrile, m.p. 53° (*Bogert*, Am. 25, 478; 26, 464). *m*- and *p*-Methyl-aminobenzoic acids,  $\text{CH}_3\text{NHC}_6\text{H}_4\text{COOH}$ , m.p. 127° and 161°, respectively, are produced by methylating the amino-acids with dimethyl sulphate, or with alkali carbonate and methyl halides; the latter reaction is of general application (*Houben*, Ber. 42, 3744; 43, 210; 46, 3833). *p*-Methylamino-benzoic acid has been synthesised by the action of carbon dioxide on methylaniline-magnesium iodide. A carbamate,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{COOMgI}$ , is first formed, but rearranges on heating, the process resembling the synthesis of salicylic acid (p. 355). In a similar way, *p*-methylamino- and *p*-ethylamino-*m*-methylbenzoic acids, m.p. 201° and 170°, respectively, are obtained from *N*-methyl- and *N*-ethyl-*o*-toluidine. By similar reactions with methyl magnesium iodide and carbon dioxide, dimethyl- and diethyl-aniline give *p*-dimethyl- and *p*-diethyl-aminobenzoic acids, m.p. 236° and 193°, respectively (*Houben*, Ber. 42, 4815). Both these acids react with permonosulphuric acid in the cold, forming sulphates of *p*-dialkyl-aminobenzoic *N*-oxides, which give *p*-dialkyl-aminobenzoic-*m*-sulphonic acids with sulphur dioxide (*Baudisch*, Ber. 51, 1048).

When methylated with methyl iodide and caustic potash, *m*- and *p*-amino-benzoic acids, as well as anthranilic acid itself, give compounds of the betaine type,



heating, isomerise to *m*- and *p*-dimethylaminobenzoic esters (*Willstätter*, Ber. 37, 414). Diethylamino-ethyl-*p*-aminobenzoate,  $\text{NH}_2[\text{C}_6\text{H}_4\{1\}\text{COOCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2 + 2\text{H}_2\text{O}$ , m.p. 51°, anhydrous 61°, is obtained by the action of ethylene chlorhydrin on *p*-nitrobenzoyl chloride, followed by reduction of the product, and transformation with diethylamine. Its monohydrochloride is used as a local anaesthetic under the name of *novocaine*, or *procaine* (*Einhorn*, Ann. 371, 125). The hydrochloride of a racemic form of *p*-amino-benzoyl- $\omega$ -dimethylamino- $\beta$ -methyl- $\gamma$ -butanol,  $\text{NH}_2\text{C}_6\text{H}_4\text{COOCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{N}(\text{CH}_3)_2$ , m.p. 213–215°, is also used as a local anaesthetic under the name *tutocaine* (*Schulemann*, Klin. Wochs. 3, 676).

**Chrysanic acid**, 3,5-dinitro-4-amino-benzoic acid,  $(\text{NO}_2)_2(\text{NH}_2) \cdot \text{C}_6\text{H}_3\text{COOH}$ , m.p. 269°, golden-yellow leaflets, is obtained by heating 3,5-dinitro-4-methoxybenzoic acid with an aqueous solution of ammonia.

**DIAMINO BENZOIC ACIDS**,  $(\text{NH}_2)_2\text{C}_6\text{H}_3\text{COOH}$ , have been obtained by the reduction of dinitro- and nitro-amino-benzoic acids. 2,4-Diaminobenzoic acid,  $(\text{NH}_2)_2[2,4]\text{C}_6\text{H}_3\text{COOH}$ , m.p. 140°, is obtained from its diaceto-compound, m.p. 261°. The latter is obtained by oxidation of diaceto-diamino-toluene (*Ullmann*, Ber. 36, 1803). When dry distilled, the diaminobenzoic acids decompose giving carbon dioxide and phenylene diamines (p. 106). Like the *o*-phenylene diamines (p. 108), the diaminobenzoic acids with amino-groups in the ortho-position readily give heterocyclic compounds; e.g., 3,4-diaminobenzoic acid, m.p. 211°, gives 3,4-aziminobenzoic acid, m.p. 270° (p. 105) with nitrous acid. *m*,*p*- and *p*,*m*-Amino-uraminobenzoic acids give two different uramino-azimino-benzoic acids, which on hydrolysis yield the same aziminobenzoic acid (*Zincke*, Ann. 291, 313, 336). 2,3-Diaminobenzoic acid, m.p. 190°, gives characteristic compounds with some sugars (*Schilling*, Ber. 34, 902).

3,4,5-Triaminobenzoic acid,  $(\text{NH}_2)_3 \cdot \text{C}_6\text{H}_2\text{COOH}$ , obtained by reduction of chrysanic acid, decomposes on heating into carbon dioxide and 1,2,3-triaminobenzene (*Salkowski*, Ann. 183, 12). 2,3,5-Triaminobenzoic acid (*Griess*, Ber. 15, 2199) is also obtained by reduction of dinitro-anthranilic acid (p. 327).

Many amino-acids derived from alkyl-benzoic acids, halogeno-amino acids, nitramino-acids, etc., have been prepared.

**AMINOPHENYL-ALIPHATIC ACIDS.** These are obtained from nitrophenyl-aliphatic acids; some are noteworthy for their tendency to form internal anhydrides, known as  $\gamma$ - and  $\delta$ -lactams. In some cases this tendency is so great that the free acids cannot be obtained, e.g., *o*-amino-hydrocinnamic acid.

**Aminophenylacetic acids**, *o*-, m.p. 119°; *m*-, m.p. 149°; *p*-, m.p. 200°.

**Aminohydrocinnamic acid**, *m*-, m.p. 84–85°; *p*-, m.p. 132°.

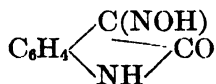
**4-Amino-3-nitro-hydrocinnamic acid**, m.p. 145° (obtained from *p*-acetamino-hydrocinnamic acid).

***p*-Aminohydratropic acid**, m.p. 128° (p. 364).

### γ- AND δ-LACTAMS OF *o*-AMINOPHENYL-ALIPHATIC

**ACIDS.** **Oxindole**, *o*-aminophenylacetic lactam,  $C_6H_4 \begin{matrix} \swarrow [1]CH_2 \cdot CO \\ \searrow [2]NH \end{matrix}$ ,

m.p. 127°, is prepared by reducing *o*-nitrophenylacetic acid with tin and hydrochloric acid, or with ferrous sulphate in alkaline solution (Heller, Ber. 49, 2774), or by reducing *dioxindole*, the lactam of *o*-amino-mandelic acid, with sodium amalgam. Baryta water at 150° decomposes oxindole into barium *o*-aminophenyl acetate; by the action of acids on the latter oxindole is re-formed (Baeyer, Ber. 16, 1704). Nitrous acid converts oxindole into β-isatoxime,



**N-Aceto-oxindole**,  $C_8H_7ON \cdot COCH_3$ , m.p. 126°, is obtained by the action of acetic anhydride on oxindole. ***o*-Acetamino-phenylacetic acid**,  $C_8H_7CO \cdot NH \cdot C_6H_4 \cdot CH_2COOH$ , m.p. 142°, is formed when acet-oxindole is dissolved in dilute sodium hydroxide, and breaks down into oxindole and acetic acid when heated with an alkali or an acid.

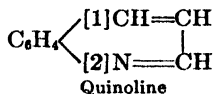
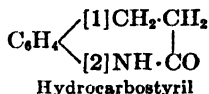
***p*-Amino-oxindole**,  $NH_2 \cdot C_6H_4NO$ , m.p. about 200°, is formed by the reduction of 2,4-dinitrophenylacetic acid (p. 320) with tin and hydrochloric acid. If ammonium sulphide is used as the reducing agent, the product is **4-amino-2-nitro-phenylacetic acid**, m.p. 185° (Gabriel, Ber. 14, 824; cf. *o*-nitro-phenyl-iso-nitroso-acetic acid).

**Atroxindole**, lactam of *o*-amino-hydratropic acid,  $C_6H_4 \begin{matrix} \swarrow [1]CH \cdot CH_3 \cdot CO \\ \searrow [2]NH \end{matrix}$ , m.p.

119°.

**Hydro-carbostyryl**, lactam of amino-hydrocinnamic acid, m.p. 163°, is formed by the reduction of *o*-nitro-hydrocinnamic acid with tin and hydrochloric acid (Glaser and Buchanan, 1869; Friedländer, Ber. 15, 2103), and also by heating hydrocarbostyryl carboxylic acid, itself obtained by the reduction of *o*-nitro-benzyl-malonic acid (Reissert, Ber. 29, 667). It may also be prepared from hyrindone oxime by the Beckmann transformation (Reissert, loc. cit.).

Hydrocarbostyryl bears the same relationship to quinoline that oxindole does to indole:



***p*-Amino-hydrocarbostyryl**,  $NH_2C_6H_4NO$ , m.p. 211°, is formed together with 4-amino-2-nitro-hydrocinnamic acid, m.p. 139°, from 2,4-dinitro-hydrocinnamic acid.

7. **DIAZOBENZOIC ACIDS** (p. 111) are produced by the action of nitrous acid on the mineral acid salts of aminobenzoic acids, in the same way as the ordinary diazonium compounds are obtained from aniline salts. The amide of *o*-aminobenzoic acid is converted by nitrous acid into *benzazimide* (p. 328). The free diazobenzoic acids are very unstable. The **diazide of anthranilic acid**,

$\text{C}_6\text{H}_5 \begin{matrix} \diagup [1]\text{CO} \\ \diagdown [2]\text{N}_2 \end{matrix} \text{O}$ , forms lustrous white needles. It is obtained by acting upon the chloride with silver oxide (*Hantzsch*, Ber. 29, 1535).

**8. DIAZOAMINO-BENZOIC ACIDS** (p. 126) are formed when nitrous fumes are passed into alcoholic solutions of aminobenzoic acids. **Diazo-*m*-aminobenzoic acid**,  $\text{COOH}[1]\text{C}_6\text{H}_4[3]\text{N}=\text{N}-\text{NH}[3']\text{C}_6\text{H}_4[1']\text{COOH}$ , is an orange-red powder. Hydrofluoric acid converts it into *m*-fluorobenzoic acid (p. 318).

**9. DIAZOIMIDO-BENZOIC ACIDS**, *azido-benzoic acids*,  $\text{N}_3\cdot\text{C}_6\text{H}_4\text{COOH}$  (p. 126), are prepared from diazo-benzoyl perbromides by the action of ammonia, or from hydrazino-benzoic acids by the action of nitrous acid. The *o*-compound, m.p. about 70°, amide, m.p. 136°, has also been isolated from products formed by the decomposition of *o*-azido-benzaldoxime with sodium hydroxide. The *m*-compound, m.p. 160° (*Bamberger*, Ber. 35, 1889, 3718); *p*-compound, m.p. 185° (*Griess*, Ber. 9, 1658).

**10. AZOXY-BENZOIC ACIDS**,  $\text{ON}_2 \begin{matrix} \diagup \text{C}_6\text{H}_4\text{COOH} \\ \diagdown \text{C}_6\text{H}_4\text{COOH} \end{matrix}$ , are prepared by reducing

nitrobenzoic acids with alcoholic potash, and then with alcoholic potassium cyanide (*Heller*, J. pr. 106, 7). The *o*-compound is also obtained by oxidising *N*-hydroxyindole-8-carboxylic acid with alkaline permanganate, or anthranil with acidified dichromate (*Heller*, J. pr. 77, 164). It may also be obtained by acting on *o*-azido-benzoic acid with sodium hydroxide (*Homolka*, Ber. 17, 1904; *Uspenski*, Ber. 24, R, 666; *Reissert*, Ber. 29, 656; *Bamberger*, Ber. 36, 374). *o*-Azoxybenzoic acid, m.p. 248° (diethyl ester, pale yellow crystals, m.p. 77°), and *p*-azoxybenzoic acid, decomp. above 300°, are formed when *o*- and *p*-nitrobenzoic acids, respectively, are reduced with zinc and alcoholic ammonium chloride solution (*Cumming*, J. Roy. Tech. Coll. Glasgow, 2, 596). The *o*-acid is also obtained from *o*-azoxytoluene (m.p. 59°) by oxidising it with potassium permanganate (*Lock*, J. pr. 138, 51). *m*-Azoxybenzoic acid, m.p. 320° (decomp.), is prepared from *m*-azoxyphenyl-propionic acid by the action of alcoholic potassium permanganate (*Reich*, Bull. 19, 146).

**11. AZOBENZOIC ACIDS**,  $\begin{matrix} \text{N}\cdot\text{C}_6\text{H}_4\text{COOH} \\ \parallel \\ \text{N}\cdot\text{C}_6\text{H}_4\text{COOH} \end{matrix}$ , are obtained from the nitro-

benzoic acids by reduction with sodium amalgam, or with zinc dust and alcoholic sodium hydroxide, and from the nitrobenzaldehydes by the action of very concentrated caustic soda (*Mair*, Ber. 34, 4132; *Freundler*, C.r. 138, 289). *o*-, *m*- and *p*-Azobenzoic acids decompose on melting. When their calcium salts are distilled, *phenazine* is formed. *o*-Azobenzoic acid, m.p. 245°, is obtained from *o*-azoxybenzoic acid (see above) by the action of zinc dust and ammonia, and subsequent oxidation with silver nitrate. Its ethyl ester forms scarlet leaflets, m.p. 85° (*Lock*, J. pr. 138, 52). Azobenzene-*o*-monocarboxylic acid,  $\text{C}_6\text{H}_5\text{N}_2[1]\text{C}_6\text{H}_4[2]\text{COOH}$ , m.p. 92°, and its homologues, are produced by condensation of *o*-nitrobenzoic acid with primary anilines. Phosphorus pentachloride converts them into  $\gamma$ -hydroxy- $\beta$ -phenylindazoles (*Freundler*, C.r. 143, 1171; 147, 981). Azobenzene-*m*-monocarboxylic acid, m.p. 171°. Azobenzene-*p*-monocarboxylic acid,  $\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4[4]\text{COOH}$ , m.p. 238°, is obtained from *p*-aminazobenzene *via* the cyanide, and from benzene-azo-*p*-toluene by oxidation with chromic acid (*Jacobson*, Ann. 303, 385). *o*-Tolyl-azobenzoic acid,  $\text{CH}_3[2]\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4[2]\text{COOH}$ , m.p. 148°, has been prepared by treating *o*-nitrotoluene with finely divided metals and caustic soda (Ger. Pat. 145,063). *m*- and *p*-Benzaldehyde-azo-*m*- and -*p*-benzoic acids,  $\text{CHOC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{COOH}$ , are obtained from *m*- and *p*-azoxybenzaldehydes (p. 277) by a rearrangement effected by concentrated sulphuric acid (*Human*, Ber. 36, 3469, 3801).

**12. HYDRAZINO-BENZOIC ACIDS.** The symmetrical hydrazo-benzoic acids are obtained from azobenzoic acids by reduction with sodium amalgam, or with ferrous sulphate and sodium hydroxide, and from nitrobenzoic acids, or their esters by means of zinc dust and acetic acid (*Krösche*, C. 1915, II, 1186). *o*-Hydrazobenzoic acid, m.p. 205°. *m*-Hydrazobenzoic acid,  $\text{COOH}[3]\text{C}_6\text{H}_4[1]\text{NH}\cdot\text{NH}[1']\text{C}_6\text{H}_4[3']\text{COOH}$ . Both these compounds rearrange to diamino-diphenyl-dicarboxylic acids (*q.v.*) on boiling with hydrochloric acid. The rearrangement of *m*-hydrazobenzoic acid to *p*-diamino-diphenic acid proves

the constitution of diphenic acid (p. 505), and consequently that of phenanthrene. *p*-Hydrazobenzene-carboxylic acid,  $C_6H_5NHNHC_6H_4[4]COOH$ , m.p.  $193^\circ$ , loses carbon dioxide and forms benzidine on rearrangement (Jacobson, Ann. 303, 384).

*o*-, *m*-, and *p*-HYDRAZINO-BENZOIC ACIDS,  $NH_2 \cdot NH \cdot C_6H_4COOH$ , are obtained by the reduction of diazobenzoic hydrochlorides and nitrates. *o*-Cyano-phenylhydrazine,  $NH_2NH[2]C_6H_4CN$ , m.p.  $153^\circ$ , is a reduction product of *o*-diazobenzonitrile, and also seems to be formed in the reduction of oximido-

dihydro-pheno- $\beta$ -triazine,  $C_6H_4 \begin{array}{c} \diagup C(OH) \cdot NH \\ | \\ N \text{-----} N \\ | \\ \diagdown \end{array}$  (Gabriel, Ber. 36, 805). Thi-

onyl-hydrazino-*o*-, *m*-, *p*-benzoic acids,  $SO:NNHC_6H_4COOH$ , m.p.  $155^\circ$ ,  $231^\circ$ , and  $258^\circ$ , respectively (Klieisen, Ber. 27, 2555). Benzylidene-*o*-hydrazino-benzoic acid,  $C_6H_5CH:NH \cdot C_6H_4COOH$ , m.p.  $224^\circ$ , is reduced by sodium amalgam to *o*-benzyl-hydrazino-benzoic acid,  $C_6H_5CH_2NHNHC_6H_4COOH$ , m.p.  $134^\circ$  (decomp.). When heated alone, or better with phosphorus oxychloride in an open vessel, *o*-hydrazino-benzoic acid gives an internal anhydride, *o*-hydrazino-

benzoic-lactazam,  $C_6H_4 \begin{array}{c} \diagup CO \\ | \\ NH \end{array} NH$ , m.p.  $242^\circ$  (decomp.), whilst when heated

with phosphorus oxychloride under pressure, chloro-indazole,  $C_6H_4 \begin{array}{c} \diagup CCl \\ | \\ N \end{array} NH$ , is formed (Fischer, Ber. 35, 2315).

### 13. PHOSPHINO-BENZOIC ACIDS. Trimethyl-phospho-*p*-benzo-betaine,

$C_6H_4 \begin{array}{c} \diagup COO^- [1] \\ | \\ p(CH_3)_3^+ [4] \end{array}$ , is obtained by oxidation of trimethyl-*p*-tolyl-phosphonium chloride with alkaline permanganate. Trimethyl-phospho-tolu-betaine is similarly prepared from trimethyl-xylyl-phosphonium chloride (Conen, Ber. 31, 2919).

### 14. Sulphobenzoic Acids

When benzoic acid is treated with sulphur trioxide in the vapour state, the chief product is the *m*-sulpho-derivative, together with a little of the *p*-acid (Remsen, Ann. 178, 279). The three monosulphobenzoic acids,  $HSO_3 \cdot C_6H_4COOH$ , can be obtained by oxidising the three toluene sulphonc acids with potassium permanganate. If, instead of the free acids, the toluene-sulphonamides are oxidised with potassium permanganate, the *m*- and *p*-sulphonamides give *m*- and *p*-sulphone-amido benzoic acids, but *o*-toluene-sulphonamide is converted into the sulphini-mide of benzoic acid, or anhydro-sulphonamino-benzoic acid, known as *saccharin*. This compound, when hydrolysed with hydrochloric acid, gives *o*-sulphobenzoic acid (Clarke, Dreger, Org. Synth. 9, 60). Both *o*- and *p*-sulphobenzoic acids are formed when potassium *m*-nitro-benzene sulphonate is boiled with aqueous potassium cyanide. The entering cyano-group does not take the place of the lost nitro-group, but enters the nucleus in a different position (cf. the formation of chlorobenzoic acids from chloro-nitrobenzenes and potassium cyanide, p. 318) (Holleman, Rec. 24, 194). When the *p*-acid is heated at  $300^\circ$ , with concentrated sulphuric acid, rearrangement into the *m*-acid takes place (Reese, Am. 54, 2009).

*o*-Sulphobenzoic acid,  $SO_3H[2]C_6H_4COOH + 3H_2O$ , m.p.  $141^\circ$  (anhyd.), resembles phthalic acid (p. 384) in its behaviour, e.g., in the formation of phthal-ins, an anhydride, and an imide. By the action of phosphorus pentachloride, two dichlorides are formed with m.p.  $40^\circ$  and  $79^\circ$ . The first is unstable, and

has the structure  $C_6H_4 \begin{array}{c} \diagup COCl \\ | \\ SO_2Cl \end{array}$ ; the other is stable, and has the structure

$C_6H_4 \begin{array}{c} \diagup CCl_2 \\ | \\ SO_2 \end{array} O$  (Scheiber, Ber. 45, 2252). On boiling with alcohols, these chlorides give the half-esters  $HSO_3C_6H_4COOR$ , with sodium ethoxide they give diethyl-*o*-sulphobenzoate, b.p.  $212^\circ$  (23 mm.); with ammonia, the asymmetrical chloride (m.p.  $79^\circ$ ) gives benzsulphonimide (see below), whereas the symmetrical,

unstable chloride gives chiefly *o*-cyano-benzene-sulphonic acid,  $\text{CN}[\text{C}_6\text{H}_4][2]\text{SO}_2\text{H}$ , m.p.  $279^\circ$ ; chloride, m.p.  $67.5^\circ$ , which is also obtained from aniline-*o*-sulphonic acid through the diazo-compound. With aniline, the chlorides form *o*-

sulphobenzoic anil,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{SO}_2 \\ \diagdown \text{CO} \end{array} \text{NC}_6\text{H}_5$ , m.p.  $190^\circ$ ; the *sym*-dianilide,  $\text{C}_6\text{H}_4\text{-(CONHC}_6\text{H}_5)_2\text{SO}_2\text{NHC}_6\text{H}_5$ , m.p.  $195^\circ$ , and the *as*-dianilide,

$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C(NHC}_6\text{H}_5)_2 \\ \diagdown \text{SO}_2 \end{array} \text{O}$ , m.p.  $270\text{--}280^\circ$  (decomp.). Both dianilides give the

dianil,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C(:NC}_6\text{H}_5) \\ \diagdown \text{SO}_2 \end{array} \text{NC}_6\text{H}_5$ , m.p.  $189^\circ$ , with phosphorus oxychloride. On

reduction, the stable chloride forms sulphobenzide (p. 263), and the unstable chloride, thiosalicylic acid,  $\text{HS}\cdot\text{C}_6\text{H}_4\text{COOH}$  (p. 360). They condense with benzene, in the presence of aluminium chloride, with the formation of *sym*-. $\text{C}_6\text{H}_5\text{CO}\cdot\text{C}_6\text{H}_5\text{SO}_2\text{C}_6\text{H}_5$ , as the chief product, the asymmetrical triphenyl-methane deriva-

tive,  $(\text{C}_6\text{H}_5)_2\text{C}\cdot\text{C}_6\text{H}_5\text{SO}_2\text{O}$ , being obtained as a by-product (*List*, Ber. 31, 1648; *Cobb*, Am. Ch. J. 35, 486). *p*-Nitro- and *p*-bromo-*o*-sulphobenzoic acids, also each give two isomeric dichlorides with phosphorus pentachloride, which show similar differences of behaviour (*Chambers*, Am. Ch. J. 30, 373; *Blanchard*, *ibid.*, 485).

*o*-Sulphobenzoic anhydride, m.p.  $118^\circ$ , is obtained from the acid by the action of acetyl chloride. It gives benzophenone-*o*-sulphonic acid,  $\text{C}_6\text{H}_4\text{COC}_6\text{H}_4\text{SO}_2\text{H}$ , with benzene and aluminium chloride (*Krannich*, Ber. 33, 3486), while the isomeric diphenyl-sulphone-*o*-carboxylic acid,  $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{COOH}$ , m.p.  $268^\circ$ , is obtained by oxidation of phenyl-*o*-tolyl-sulphone (*Canter*, Am. Ch. J. 25, 96).

*o*-Carbomethoxy-benzene-sulphonyl chloride,  $\text{ClSO}_2\cdot\text{C}_6\text{H}_4\text{COOCH}_3$ , m.p.  $65^\circ$ , is obtained by the action of chlorine on *o*-carbomethoxy-benzene sulphinic acid,  $\text{HSO}_2\cdot\text{C}_6\text{H}_4\text{COOCH}_3$ , m.p.  $99^\circ$ . The latter is prepared by diazotising anthranilic ester, and then replacing the diazo-group by the sulphino-group (Ger. Pat. 124,407).

*o*-Sulphonamido-benzoic acid,  $\text{NH}_2\text{SO}_2[2]\text{C}_6\text{H}_4[1]\text{COOH}$ , m.p.  $153\text{--}155^\circ$ , changes to the sulphonimide at the melting point. Methyl- and ethyl esters, m.p.  $119^\circ$  and  $84^\circ$ , respectively (Ger. Pat. 101,483). The acid has been prepared by oxidising *o*-toluene-sulphonamide with potassium ferricyanide (*Noyes*, Am. Ch. J. 8, 167), and from its internal anhydride by the action of warm caustic alkali. The isomeric *o*-sulphobenzamide,  $\text{C}_6\text{H}_4(\text{CONH}_2)\text{SO}_2\text{H}$ , m.p.  $194^\circ$ , is formed when sulphobenzoic acid is fused with ammonium thiocyanate. It gives *o*-sulphanilic acid with potassium hypobromite (Ger. Pat. 84,666).

*o*-Anhydro-sulphonamido-benzoic acid, *o*-benzsulphinimide,

$\text{C}_6\text{H}_4 \begin{array}{c} \diagup [1]\text{CO} \\ \diagdown [2]\text{SO}_2 \end{array} \text{NH}$ , m.p.  $220^\circ$ , is known as **saccharin**. It was discovered by

*Remsen* and *Fahlberg* in 1879. Its preparation has been described above. It is also obtained by treating the reaction product from *o*-sulphobenzaldehyde and phosphorus pentachloride with ammonia, followed by oxidation with air (Ger. Pat. 94,948), and by heating *o*-sulphinobenzoic acid (see above) with hydroxylamine (*Gattermann*, Ber. 32, 1144). For more recent methods see *Halla*, Z. Elektroch. 36, 96, and *Herzog*, Chem. Ztg. 57, 575. Saccharin is manufactured industrially in considerable quantities, and is used for sweetening, being 500 times as sweet as cane sugar. A bitter-tasting product, saccharin-(*o*-tolyl-3-sulphonyl-imide),  $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}_2\text{S}_2$ , is formed in the manufacture of saccharin. It melts at

$255^\circ$ , and its constitution is  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C:NSO}_2\text{C}_6\text{H}_4\text{CH}_3 \\ \diagdown \text{SO}_2 \end{array} \text{NH}$ . This substance has been

prepared synthetically by careful oxidation of *o*-toluene-sulphonamide, and it may also be obtained from pseudo-saccharin chloride (see below), and from *o*-toluene-sulphonamide by other methods (*Klages*, J. pr. 116, 163).

Saccharin is difficultly soluble in water, and resembles succinimide and phthalimide in behaving as a strong acid. It forms imino-salts, *e.g.*, a sodium salt,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO}[1] \\ \diagdown \text{SO}_2[2] \end{smallmatrix} \text{NNa}$ , which is readily soluble in water, and is 400 times as sweet as cane sugar. For its physiological effect, see *Herzog*, Chem. Ztg. 57, 575. It is the anion which is responsible for the sweet taste (*Taeufel*, Ber. 58, 909; *Oddo*, Gazz. 57, 465). For the taste of saccharin and related compounds, see *Holleman*, Rec. 42, 839; Acad. Amsterdam 33, 307.

Halides, such as benzyl chloride and acetyl chloride, readily react with saccharin to form N-derivatives. With phosphorus pentachloride at 180°, pseudo-saccharin chloride,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CCl}[1] \\ \diagdown \text{SO}_2[2] \end{smallmatrix} \text{N}$ , m.p. 149°, is obtained, while at 70–75°, o-cyano-benzene-sulphochloride is formed (*Walker*, J. 89, 350). Treatment with

phosphorus sulphide at about 200°, gives thiosaccharin,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CS} \\ \diagdown \text{SO}_2 \end{smallmatrix} \text{NH}$ , m.p. 180°, golden yellow needles, with an intensely bitter taste (*Mannessier*, Gazz. 45, I, 450). Saccharin condenses with phenols and aminophenols, to give *saccharcins*. These compounds are dyestuffs, resembling phthaleins (*Sisley*, Bull. [3], 17, 821; Ger. Pat. 100, 779). *Sulpham-phthaleins* are also formed (*Dutt*, J. 121, 2389). For the formation of thiazole derivatives from saccharin derivatives and hydroxylamine, see *Mannessier*, Gazz. 62, 1067.

All those sulpho-acids, which are derived from alkyl-benzoic acids, and in which the sulpho-group occupies the o-position to the carboxyl group, are capable of forming *pulphonimides*, and *sulpho-carboxylic amides*. For esters and half-esters of o- and p-sulphobenzoic acids, see *Wegscheider*, Mo. 23, 1093. For p-sulphamido-benzoic acid and its derivatives see *Stoddart*, Am. Ch. J. 47, 1; *Chamberlain*, Am. Ch. J. 47, 318.

3,5-Disulphobenzoic acid is formed when benzoic acid and fuming sulphuric acid containing 70% of sulphur trioxide are heated to 250° in a sealed tube. 2,4-Disulphobenzoic acid is obtained from toluene-2,3-disulphonic acid (*Fahlberg*, Ber. 14, 1205).

Diphenyl-sulphone-o-carboxylic acid,  $\text{C}_6\text{H}_5\text{SO}_2[2]\text{C}_6\text{H}_4[1]\text{COOH}$ , m.p. 144°, is obtained by oxidising phenyl-o-tolyl-sulphone, or phenyl-thiosalicylic acid (p. 361) with potassium permanganate, or by heating the potassium salts of o-chlorobenzoic acid and benzene-sulphinic acid in aqueous or amyl alcohol solution in the presence of copper. It is converted into *benzophenone-sulphone*

$\text{C}_6\text{H}_5 \begin{smallmatrix} \diagup \text{SO}_2 \\ \diagdown \text{CO} \end{smallmatrix} \text{C}_6\text{H}_5$  (p. 520) by the action of hot concentrated sulphuric acid (*Ullmann*, Ber. 38, 729; *Weedon*, Am. J. 33, 336).

Benzene-1-carboxylic-2-selenonic acid,  $\text{C}_6\text{H}_4(\text{COOH})\text{SeO}_3\text{H}$ , formed from diphenyl-diselenide-dicarboxylic acid (p. 361), has not yet been obtained in a crystalline form. With hydrogen chloride it yields benzene-1-carboxylic-2-seleninic acid,  $\text{C}_6\text{H}_4(\text{COOH})\text{SeO}_2\text{H}$ , which melts at 228–229°, with anhydride formation (*Lesser*, Ber. 46, 2643).

## 1b. MONOHYDRIC HYDROXY-PHENYL ALIPHATIC ALCOHOLS AND THEIR OXIDATION PRODUCTS

### 1. Monohydric Hydroxy-phenyl Aliphatic Alcohols, or Phenol Alcohols

The monohydric phenol alcohols contain one alcoholic hydroxyl group and one or more hydroxyl groups attached to the benzene ring, the latter giving them phenolic properties. Some alcohols belonging to this group are obtained by simple transformations of well-known vegetable substances. A number of mono-, di-, and tri-hydroxy-phenylethylamines are of special interest on account of their strong physiological effects and their occurrence in the vegetable and animal

kingdoms (see *p*-hydroxy-phenylethylamine, hordenine, and mezcaltine). Some hydroxy-phenyl-aliphatic alcohols, saligenin, for example, are local anaesthetics (*Hirschfelder*, *J. Pharm.* 15, 261).

**Preparation.**—Some of the methods of formation given for the benzyl alcohols (p. 249) apply to the phenol alcohols as well: (1) the reduction of the corresponding aldehydes and ketones; (2) the treatment of aldehydes with aqueous alkalis; and (3) of amides with sodium amalgam (*Hutchinson*, *Ber.* 24, 175). (4) They are connected with the benzyl alcohols by means of the amino-phenyl-paraffin alcohols, the latter being converted into hydroxy-phenyl-paraffin alcohols by nitrous acid. (5) Phenol alcohols (and phenol-aldehydes and phenol-carboxylic acids) are obtained from cresols and their homologues, of which the hydroxyl groups have been protected by esterification with inorganic acids; they are chlorinated, step by step, at 180°, and finally chlorine is replaced by OH (*Ger. Pat.* 233,631). Phenol alcohols are obtained by *nuclear synthesis* by the following methods: (6) by the action of methylene chloride on phenols (*Greene*, *C.r.* 90, 40), or by the action of formaldehyde and sodium hydroxide on phenols (*Manasse*, *J. pr.* [2], 50, 225). Phenols and phenol ethers with so-called negative substituents, such as NO<sub>2</sub>, Cl, CHO, COOH, condense with formaldehyde and hydrochloric acid to give hydroxy-benzyl chlorides, in which chlorine is very readily replaced by OH or OR (*Stoerner*, *Ber.* 34, 2455; *Eichengrün*, *C.* 1902, II, 894); frequently two CH<sub>2</sub>Cl groups enter the ring in the meta-position (*Br. Pats.* 347,887 and 347,892); (7) by the action of alkyl-magnesium halides on phenol-carboxylic esters. Acylated hydroxy-benzylamines can be synthesised by condensing *N*-methylol-acylamides, RCONHCH<sub>2</sub>OH, with phenols (*Einhorn*, *Ann.* 343, 215), a method resembling closely method 6 above.

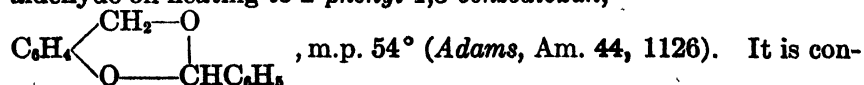
**MONOHYDROXY-BENZYL ALCOHOLS.** Three isomers are theoretically possible, and all three have been prepared by reducing the corresponding aldehydes with sodium amalgam. The best known of them is *o*-hydroxy-benzyl alcohol, or *saligenin*. The m.p. of the isomers are *o*- 86°, *m*- 67°, *p*- 110°.

*Saligenin*, *o*-hydroxy-benzyl alcohol, was first obtained by *Piria* (*Ann.* 56, 37) in 1845, by decomposing the glucoside *salicin* (*Vol. II*, p. 355) with *emulsin*, *ptyalin*, or dilute acids, glucose being eliminated:



*Saligenin* has been prepared from salicylaldehyde, salicylamide, *o*-amino-benzyl alcohol, and phenol, by the general methods described above. For its preparation by the electrolysis of salicylic acid in the presence of magnesium butyrate, see *Rutovski*, *Pharm. Moscovia*, 1928, and from amino-benzyl alcohol, see *Reissert*, *Ber.* 61, 2555.

It is readily soluble in alcohol, ether, and hot water. The solutions give a deep-blue colour with ferric chloride. It condenses with benzaldehyde on heating to 2-phenyl-1,3-benzodioxan,





verted by acids into a resinous substance, *saliretin*. The theory of this reaction has been discussed by *Baekeland* (Ind. Eng. 17, 225). Ethers and substitution products of saligenin have been prepared, some of them from the corresponding salicylic derivatives. The *d*, $\beta$ -galactoside of saligenin, m.p. 215–218°, has been obtained by *Helfferrich* (Ber. 65, 408) from aceto-bromo-galactose and *o*-cresol, by brominating in the light, replacing the bromine by hydroxyl, and finally eliminating the acetyl group.

*o*-Hydroxyl-benzylamine, *salicylamine*, m.p. 121° (*Goldschmidt*, Ber. 23, 2744). *o*-Mercapto-benzyl alcohol, HS[2]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>OH, benzoate, m.p. 125–126°, has been obtained together with saligenin and *o*-benzyl alcohol sulphide, S(C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OH)<sub>2</sub>, m.p. 164°, from diazobenzyl alcohol, through the xanthate, by the action of caustic potash (*Reissert*, Ber. 61, 2555). *o*-Hydroxy-benzyl-aniline, m.p. 138°, can be obtained by the combination of anhydroformaldehyde-aniline (p. 84) with phenol (Ger. Pat. 109,498). The *O*-acetyl compounds of *o*-hydroxy-benzylamines and -anilines are unstable and change spontaneously into the isomeric *N*-acetyl compounds (*Auwers*, Ann. 332, 159; cf. p. 205). In the acetylation of *o*-hydroxy-benzylamines steric hindrance has been observed (*Paal*, Ber. 32, 2057). *p*-Hydroxy-benzyl mustard oil, *sinalbin mustard oil*, HO[4]C<sub>6</sub>H<sub>4</sub>[1]NCS occurs as a glucoside in white mustard seed.

Anise-alcohol, *p*-methoxy-benzyl-alcohol, CH<sub>3</sub>O[4]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>OH, m.p. 45°, b.p. 259°, occurs in certain vanillas (e.g., from Tahiti; *Schimmel's* Ber. 1909, II, 141), and is obtained by the action of alcoholic potash on anisaldehyde, or by the catalytic reduction of the latter. When oxidised anisaldehyde is re-formed. *p*-Methoxy-benzylamine, *anisylamine*, CH<sub>3</sub>O[4]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>NH<sub>2</sub>, b.p. 236–237° is prepared by the action of sodium amalgam on anisaldoxime in acetic acid (*Tiffeneau*, Bull. 9, 819).

*p*-Homosaligenin, CH<sub>2</sub>[5]C<sub>6</sub>H<sub>3</sub>[2](OH)CH<sub>2</sub>OH, m.p. 205°, is obtained from *p*-cresol by method 6, p. 335 (*Ullmann*, Ber. 42, 2539). *p*-Thymotin-alcohol, CH<sub>3</sub>[2]C<sub>6</sub>H<sub>7</sub>[5]C<sub>6</sub>H<sub>4</sub>[4]OH[1]CH<sub>2</sub>OH, m.p. 120° (*Manasse*, Ber. 27, 2412).

*o*-Hydroxy-phenyl-ethyl alcohol, HO[2]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>CH<sub>2</sub>OH, b.p. 169° (12 mm.), is formed, together with *o*-hydroxy-phenyl-acetic acid, when coumarone,

C<sub>6</sub>H<sub>4</sub> $\begin{matrix} \text{[1]CH} \\ \text{[2]O} \end{matrix}$ CH, is acted upon by alcoholic potash. The bromide of this alcohol is converted by sodium hydroxide into a cyclic-phenol-alcohol ether, the so-called *hydrocoumarone*, C<sub>6</sub>H<sub>4</sub> $\begin{matrix} \text{[1]CH}_2 \\ \text{[2]O} \end{matrix}$ CH<sub>2</sub>, b.p. 188°. This compound can

also be obtained by reducing coumarone with sodium and alcohol, and by condensing bromoethyl-*o*-bromophenyl ether, BrC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>·CH<sub>2</sub>Br, by means of sodium (*Stoermer*, Ber. 36, 2873).

*o*-Hydroxy-phenyl-ethylamine, HO[2]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, hydrochloride, m.p. 153°, is a degradation product of melilotic hydrazide. Methyl iodide converts this base into a quaternary methiodide, m.p. 218°, which loses trimethylamine on heating with sodium hydroxide, and gives *hydrocoumarone* (see above) (*Pschorr*, Ber. 38, 2067).

$\beta$ -(*o*-Hydroxy-phenyl)-ethyl-dimethyl-amine, *o*-hordenine, HO[2]C<sub>6</sub>H<sub>4</sub>[1]-CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>, b.p. 136–137° (13 mm.), is made by treating *o*- $\beta$ -chloroethyl-benzanilide with dimethylamine, eliminating the benzoyl group, diazotising, and boiling with water (*Braun*, Ber. 57, 913). *p*-Hydroxy-phenyl-methylamine, b.p. 234–236°, is obtained by the action of potassium cyanide and hydrochloric acid on *p*-hydroxy-benzaldehyde-bisulphite, and reducing the nitrile produced with zinc and hydrochloric acid (C. 1911, I, 580).

*p*-Hydroxy-phenyl-ethyl alcohol, tyrosol, HO[4]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>·CH<sub>2</sub>OH, m.p. 93°, b.p. 195° (18 mm.), has been prepared by the action of potassium nitrite on the hydrochlorides of *p*-hydroxy-phenyl-ethylamine, or *p*-amino-phenyl-ethylamine, or *p*-amino-phenyl-ethyl alcohol (*Ehrlich*, Ber. 45, 2428). Its chloride reacts with dimethylamine to give hordenine (see below) (*Pistshimuah*, J. Russ.

48, 1). Fungi convert hordenine into tyrosol. It is also produced by bacterial action (Ehrlich, Bioch. Z. 75, 417; Hirai, Acta Kyoto, 1916).

***p*-Hydroxy-phenyl-ethylamine**, tyramine,  $\text{HO}[4]\text{C}_6\text{H}_4[1]\text{CH}_2\text{CH}_2\text{NH}_2$ , m.p. 165–166°, hydrochloride, m.p. 290°, is one of the active principles of ergot, in which it occurs together with  $\beta$ -imidazyl-ethylamine, and ergotoxin. It is also found in *Capsella bursa pastoris*, and in the poison from the salivary glands of some arthropods. Like *adrenaline* (Vol. II, p. 579), to which it is closely related, tyramine raises the blood pressure, and stimulates respiration. It is formed when tyrosin, one of the principal degradation products of albumin, is heated, or decays, carbon dioxide being liberated. It is obtained synthetically by reduction of *p*-hydroxybenzyl cyanide, or anisylidene-nitromethane,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_4[1]\text{CH}:\text{CHNO}_2$ ; in the latter case hydrolysis is subsequently effected with hydriodic acid (Rosenmund, Ber. 42, 4778). Another process is to nitrate  $\beta$ -phenyl-ethylbromide, couple the *p*-nitro-compound obtained with hexamethylene-tetramine (Vol. I, p. 248), and decompose the double compound thus formed with hydrochloric acid. This gives  $\beta$ -(*p*-nitrophenyl)-ethylamine hydrochloride, m.p. 214°; the stannic chloride compound of this is diazotised, and tyramine is the final product (Slotta, Ber. 64, 1519). For other syntheses, see Arch. Pharm. 270, 345. Tyramine, alone, or mixed with  $\beta$ -imidazyl-ethylamine, is used in obstetrics.

***p*-Methoxy-phenyl-ethylamine**, *tyramine methyl ether*,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_2$ , is an oil; its hydrochloride melts about 160°. It is obtained from *p*-methoxy-phenyl-acetaldoxime and nitromethane, and reducing the resulting  $\omega$ -nitrophenol to the amine (Ger. Pat. 230,043). On methylation, followed by hydrolysis of the methoxy-group by hydriodic acid (Pistshimuka, J. Russ. 48, 1) it gives:

**$\beta$ -(*p*-Hydroxy-phenyl)-ethyl-dimethylamine**, *hordenine*, or *anhaline*,  $\text{HO}[4]\text{C}_6\text{H}_4[1]\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ , m.p. 118°, a base. This substance is the active principle of malt (Rosenmund, Ber. 43, 306), and has also been detected among the alkaloids extracted from certain Mexican cacti of the genus *Anhalonium* (Späth, Mo. 40, 129). It has been synthesised by Voswinckel (Ber. 45, 1004), by treating *p*- $\omega$ -chloromethyl-anisyl ketone with dimethylamine, demethylating and replacing the keto-oxygen by hydrogen; by Ehrlich (Ber. 45, 2428) by the action of dimethylamine on *p*-hydroxy-phenyl-ethyl chloride; and from anisaldehyde through *p*-methoxy-phenyl-acetonitrile (Ar. Pharm. 271, 441). Higher homologues of hordenine, with longer aliphatic chains, viz., *p*-hydroxy-phenyl-propyl-, -butyl-, and -amyl-dimethylamine, have been prepared (Braun, Ber. 45, 2504).

***p*-(*p'*-Hydroxy-phenyl-oxy)- $\beta$ -phenyl-ethylamine**, *tyronamine*,  $\text{HO}[4]\text{C}_6\text{H}_4[1] \cdot \text{O} \cdot [4]\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_2$ , m.p. 136.5°, the parent substance of thyroxin (Vol. II, p. 582) has been obtained from *p*-(*p'*-methoxy-phenoxy)-nitrobenzene (Stohr, Z. physiol. Ch. 201, 142). ***p*-Hydroxy-phenyl-isopropylamine**,  $\text{HO}\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_3$ , m.p. 126°, is prepared by reducing *p*-hydroxy-phenyl-acetoxime (Mannich, Ber. 43, 192). ***o*-Hydroxy-phenyl-ethyl carbinol**,  $\text{HO}[2]\text{C}_6\text{H}_4\text{CH}(\text{OH})\text{C}_2\text{H}_5$ , b.p. 125–130° (0.25 mm.), is obtained by reduction of *o*-hydroxy-phenyl-ethyl ketone, or synthetically by the action of zinc ethyl on tetracetylhelicin (Vol. II, p. 355) (Fischer, Ber. 36, 2575). ***o*-Hydroxy-phenyl-diethyl carbinol**,  $\text{HO}[2]\text{C}_6\text{H}_4\text{C}(\text{OH})(\text{C}_2\text{H}_5)_2$ , m.p. 57°, obtained from ethyl salicylate and ethyl magnesium iodide, readily loses water, becoming an olefin-phenol (Mounie, Bull. [3], 29, 350).

***o*-Chloro-*p*-hydroxy-benzyl- and *p*-chloro-*o*-hydroxy-benzyl-alcohol**,  $\text{ClC}_6\text{H}_4(\text{OH})\text{CH}_2\text{OH}$ , and ***o*-nitro-*p*-hydroxy-benzyl- and *p*-nitro-*o*-hydroxy-benzyl alcohols** are obtained by the action of formaldehyde and halogen hydrides on chloro- and nitro-phenol; the halogen esters first formed are very readily hydrolysed (cf. pseudophenol halides, p. 339). ***p*-Amino-saligenin**,  $\text{NH}_2[4]\text{C}_6\text{H}_4[2]\text{OH}[1]\text{CH}_2\text{OH}$ , is made by reduction of *p*-nitro-*o*-hydroxy-benzyl alcohol. It is used as a developer in photography under the name of Edinol (Stormer, Ber. 34, 2455; Ger. Pat. 136,680).

**DIHYDROXY-BENZYL ALCOHOLS.** While free dihydroxy-benzyl alcohols are very unstable, e.g., 2,3-dihydroxy-benzyl alcohol (Ar. Pharm. 264, 448), derivatives of 2,3-, 2,5-, 3,4- and 3,5-dihydroxy-benzyl alcohols have been obtained by the reduction of aldehyde ethers with sodium amalgam, and by catalytic hydrogenation of carbomethoxylated acid chlorides and aldehydes. The derivatives of di-( $\beta$ -phenyl-ethyl)-amine, and of benzyl- $\beta$ -phenyl-ethylamine

with two hydroxyl groups in the 3,4-position, are of pharmacological interest (*Buck, Am. 53, 2192*).

**Vanillyl alcohol**,  $\text{CH}_3\text{O}[3]\text{HO}[4]\text{C}_6\text{H}_3[1]\text{CH}_2\text{OH}$ , m.p.  $115^\circ$ , is a reduction product of *vanillin* (p. 347). **Piperonyl alcohol**,  $\text{CH}_3\text{O}[4]\text{O}[3]\text{C}_6\text{H}_3[1]\text{CH}_2\text{OH}$ ,

m.p.  $57^\circ$ , is obtained from piperonal by Cannizzaro's reaction, by electrochemical reduction in sodium carbonate solution, and by the action of sodium methoxide at  $100^\circ$  (*Braxin, Ber. 63, 489*). ***p*-Veratryl alcohol**,  $(\text{CH}_3\text{O})_2[3,4]\text{C}_6\text{H}_3[1]\text{CH}_2\text{OH}$ , b.p.  $168\text{--}170^\circ$ , is prepared by catalytic reduction of the aldehyde (Ger. Pat. 515,332); and ***o*-veratryl alcohol**  $(\text{CH}_3)_2[2,3]\text{C}_6\text{H}_3[1]\text{CH}_2\text{OH}$ , m.p.  $50^\circ$ , is obtained by catalytic reduction of the *o*-aldehyde with platinum oxide in acetic acid (*Kaufmann, Ber. 51, 123*). **Homopiperonyl alcohol**,  $\text{CH}_3\text{O}[3]\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{OH}$ ,

b.p.  $156^\circ$  (10 mm.) (*Semmler, Ber. 41, 2752*). **Dimethyl-gentisinal alcohol**,  $(\text{CH}_3\text{O})_2[2,5]\text{C}_6\text{H}_3[1]\text{CH}_2\text{OH}$ , b.p.  $278^\circ$ .

**2,3-Dihydroxy-benzylamine**,  $(\text{HO})_2[2,3]\text{C}_6\text{H}_3\text{CH}_2\text{NH}_2$ , hydrochloride, m.p.  $186^\circ$ , is obtained from *o*-veratraldehyde oxime (see above) by reduction, and subsequent removal of methyl groups. The 3,4-compound, hydrochloride, m.p.  $172^\circ$ , is obtained by a similar method from *p*-veratraldehyde (p. 349) (*Douletleau, Bull. 9, 932*). **Vanillylamine**,  $(\text{HO})[4](\text{CH}_3\text{O})[3]\text{C}_6\text{H}_3[1]\text{CH}_2\text{NH}_2$ , m.p.  $145\text{--}146^\circ$ , is obtained by reducing vanillin oxime or by decomposing *capsaicin*, the vanillyl-amide of  $\Delta^6$ -isodecylenic acid:  $(\text{HO})[4](\text{CH}_3\text{O})[3]\text{C}_6\text{H}_3[1]\text{CH}_2\text{NH}\cdot\text{CO}(\text{CH}_2)_4\text{CH}:\text{CHCH}(\text{CH}_3)_2$ , m.p.  $65^\circ$ , of which Cayenne pepper contains about 0.25%. It is the principle causing the "hot" taste (*Lapworth, J. 115, 1109; Gibson, J. 123, 1269; cf. Vol. II, p. 405*). For vanillyl amides of other acids, see *Oll, Ann. 425, 314; Nelson, Am. 41, 2121; Jones, J. 127, 2588; Kobayashi, Scient. Japan. 6*. **Homopiperonyl-amine**,  $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{NH}_2$ , b.p.  $166^\circ$  (20 mm.), and **homoveratryl-amine**,  $(\text{CH}_3\text{O})_2[3,4]\text{C}_6\text{H}_3[1]\text{CH}_2\text{CH}_2\text{NH}_2$ , b.p.  $155^\circ$  (12 mm.), are obtained by catalytic reduction of 3,4-methylene-dioxy- and 3,4-dimethoxy-acetyl-mandelic nitriles, respectively (*Arch. Pharm. 269, 75*).

**Methyl-guaiacyl-carbinol**, *apocynol*,  $(\text{HO})[4](\text{CH}_3\text{O})[3]\text{C}_6\text{H}_3[1]\text{CHOHCH}_3$ , m.p.  $101^\circ$ , benzoate, m.p.  $128^\circ$ , is prepared by the action of methyl magnesium iodide on vanillin benzoate (*Arch. Pharm. 269, 334*). **Methyl-guaiacyl-ethyl-carbinol**,  $(\text{HO})[4](\text{CH}_3\text{O})[3]\text{C}_6\text{H}_3[1]\text{CH}_2\text{CH}_2\text{CHOHCH}_3$ , b.p.  $197^\circ$  (17 mm.), is the carbinol corresponding to the ketone zingerone (p. 353), from which it is obtained by reduction with sodium and alcohol. It has the same hot taste as the ketone (*Nomura, Rep. Tohoku, 1925*).

**3,4-Dihydroxy-phenyl-ethyl-amine**,  $(\text{HO})_2[3,4]\text{C}_6\text{H}_3[1]\text{CH}_2\text{CH}_2\text{NH}_2$ , hydrochloride, m.p.  $174\text{--}175^\circ$ , is obtained by the reduction of the corresponding nitro-styrol (Ger. Pat. 247,906), and from amino-tyramine (*Waser, Helv. 6, 54*).

**$\beta$ -(3,4-Dihydroxy-phenyl)-ethyl-methylamine**, *epinine*,  $(\text{HO})_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{NHCH}_3$ , m.p.  $177^\circ$ , hydrochloride, m.p.  $179\text{--}180^\circ$ , is prepared from veratraldehyde (p. 349) through the corresponding hydrocinnamic ester; the acid amide is reduced, and the two methyl groups are eliminated. For other syntheses, e.g., from dimethoxy-acetophenone, see *Arch. Pharm. 270, 348*. It is a styptic, and raises the blood pressure.

**TRIMETHOXY-BENZYL ALCOHOLS**. **5-Methoxy-3,4-methylene-dioxy-benzylamine**,  $(\text{CH}_3\text{O})[5](\text{CH}_2\text{O})_2[3,4]\text{C}_6\text{H}_3[1]\text{CH}_2\text{NH}_2$ , b.p.  $172.5^\circ$  (16.5 mm.) is obtained by reducing myristicin aldehyde oxime (p. 350) in 50% acetic acid, with zinc dust (*Rugheimer, Ber. 45, 1340*).

**$\beta$ -(3,4,5-Trimethoxy-phenyl)-ethylamine**, *mezcaline*,  $(\text{CH}_3\text{O})_3\text{C}_6\text{H}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , b.p.  $35\text{--}36^\circ$ , b.p.  $180^\circ$  (12 mm.), occurs, together with other bases, in Mexican cacti belonging to the *Anhalonium* genus. It has been prepared synthetically from trimethyl-gall-aldehyde (p. 350), by addition of nitromethane, followed by reduction from trimethyl-gallyl alcohol, through the chloride and the cyanide, followed by reduction (Ger. Pat. 526,172; Br. Pat. 339,699); from trimethyl-homogall-aldehyde (from *elemicin*, p. 454), through the oxime and the nitrile by reduction (*Hahn, Ber. 57, 696*); from 3,4,5-trimethoxy- $\omega$ -nitrostyrene by reduction (*Slotta, J. pr. 137, 340*); and from trimethoxy-phenyl-propionamide by the action of sodium hypobromite (*Slotta, Ber. 63, 3029; Skita, Ber. 65, 431*). It is a powerful poison, acting on the nerve centres and causing hallucinations.

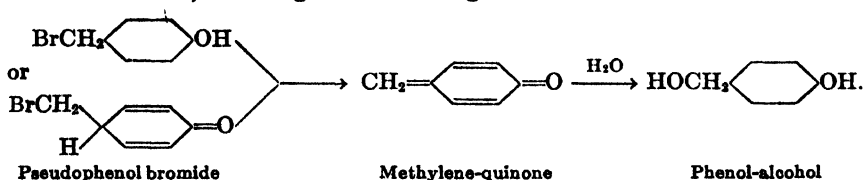
Hydrochloride, m.p. 184–195°. Isomers, analogues, and homologues of mezeoline have been studied by Jansen, Weekbl. 26, 421; Rec. 50, 291; see also Ar. Pharm. 270, 410; Hahn, Ber. 67, 1486.

*Pseudophenol Halides, Methylene Quinones, and Quinols*

**PSEUDOPHENOL-ALCOHOL HALIDES.** Certain halogen esters of phenol-alcohols behave in a rather remarkable manner. This is particularly the case with those *o*- and *p*-hydroxy-benzyl bromides and chlorides in which nuclear hydrogen is replaced by chlorine or bromine. These compounds are obtained: (1) by the action of hydrobromic acid on phenol-alcohols; (2) by the addition of hydrogen bromide or bromine to vinyl-phenols; (3) by suitable bromination of *o*- or *p*-alkyl-phenols. The following is a list of the more important of these compounds:

- o*-Hydroxymesityl chloride,  $C_6H_2[3,5](CH_2)_2[2,1](OH)CH_2Cl$ , m.p. 58°.  
*o*-Hydroxyisoduryl chloride,  $C_6H[3,5,6](CH_2)_3[2,1](OH)CH_2Cl$ , m.p. 100°.  
*m*-Bromo-*o*-hydroxybenzyl bromide,  $C_6H_3[3]Br[2,1](OH)CH_2Br$ , m.p. 98°.  
*m,m*-Dibromo-*o*-hydroxybenzyl bromide,  $C_6H_2[3,5]Br_2[2,1](OH)CH_2Br$ , m.p. 117°.  
Tribromo-*o*-hydroxybenzyl bromide,  $C_6HBr_3[2,1](OH)CH_2Br$ , m.p. 134°.  
Tetrabromo-*o*-hydroxybenzyl bromide,  $C_6Br_4[2,1](OH)CH_2Br$ , m.p. 156°.  
Dibromo-*o*-hydroxymesityl bromide,  $C_6Br_2(CH_2)_2[2,1](OH)CH_2Br$ , m.p. 150°.  
Bromo-*o*-hydroxyisoduryl bromide,  $C_6Br(CH_2)_3[2,1](OH)CH_2Br$ , m.p. 112°.  
*m,m*-Dibromo-*p*-hydroxybenzyl bromide,  $C_6H_2Br_2[4,1](OH)CH_2Br$ , m.p. 150°.  
Dibromo-*p*-hydroxypseudocumyl bromide,  $C_6Br_2(CH_2)_2[4,1](OH)CH_2Br$ , m.p. 126°.  
Dibromo-*p*-hydroxymesityl bromide, m.p. 147°.  
Tetrachloro-*p*-hydroxybenzyl bromide,  $C_6Cl_4[4,1](OH)CH_2Br$ , m.p. 160°.  
Tetrachloro-*p*-hydroxybenzyl chloride, m.p. 146°.  
Penta-, hexa-, and heptabromo-*p*-ethyl phenol,  $C_6HBr_5[4,1](OH)C^*HBr-CH_2Br$ ,  $C_6HBr_4[4,1](OH)C^*HBrCHBr_2$ , and  $C_6Br_3[4,1](OH)C^*HBrCHBr_2$ .  
Dibromoisoeugenol dibromide,  $C_6HBr_2[3]OCH_3[4,1](OH)C^*HBrCHBrCH_3$ .  
Heptabromo-*p*-isopropyl-phenol,  $C_6Br_4[2,1](OH)C^*HBr(CHBr_2)CH_3$ , m.p. 183°, etc.

These substances are insoluble in alkalis. One of the aliphatic halogen atoms is very mobile, and is readily replaced by OH, OAlk, OCOCH<sub>3</sub>, NHR, CN, or SH, on treatment with water, alcohol, acetic acid, amines, potassium cyanide, and potassium hydrogen sulphide, respectively. With phenols, and with tertiary amines of the dimethylaniline type, diphenylmethane derivatives are formed. This reaction takes place very readily, and no condensing agent is necessary. The thiocyanates and acetates of the pseudophenols are as reactive as the halides, as are also certain nitro-compounds, such as  $C_6Br_2(CH_2)_2[4,1](OH)CH_2NO_2$  (Auwers, Ber. 34, 4264; cf. the similar behaviour of propenyl-phenol dibromides). The name "*pseudo-phenols*" has been given to these substances on account of their insolubility in alkalis. Their behaviour is explained by assuming that the  $CH_2Br$  and  $CHBr$  groups are drawn very near the *p*- or *o*-hydroxy groups, by some mechanism not yet understood, and that therefore hydrogen bromide is easily split off with the formation of highly reactive *methylene-quinones*, or "*quinomethanes*" (Bistrzycki, Ber. 36, 2336). In most cases these would be intermediate compounds, which then add on the reagents mentioned above. Another explanation attributes a quinone structure to the pseudophenol bromides themselves, according to the following scheme:



Otherwise the pseudophenols behave in just the same way as the phenols. They are readily converted into O-acetyl compounds and urethanes.

**METHYLENE QUINONES.** The methylene quinones, which are supposed to be intermediate compounds in the reactions of the pseudophenol halides, can be prepared by treating *o*- and *p*-pseudophenol bromides with aqueous sodium acetate or dilute alkali. The *o*-methylene quinones are easily obtained, but the *p*-methylene quinones from the simpler pseudophenol bromides have not yet been isolated, since they readily change, partly into polymers insoluble in alkali, and partly into condensation products which dissolve in alkali, e.g., *p,p'*-dihydroxy-diphenylmethane derivatives. Derivatives of *p*-ethylidene-quinone, *p*-propylidene-quinone, and *p*-*iso*-propylidene-quinone, however, have been prepared from the pseudobromides of *p*-ethyl-phenol, isoeugenol, and *p*-*iso*-propyl-phenol (see above). The methylene-quinones are yellow, and readily change into colourless polymerides under the influence of light or acids. There is a striking difference between the chemical behaviour of the *o*- and *p*-methylene-quinones. The *p*-compounds are highly reactive, and readily combine with water, alcohols, acetic acid, and hydrogen halides to form phenol-alcohol derivatives, but *o*-methylene-quinones do not react at all with these reagents, so that they can hardly be intermediate compounds in the reactions of the pseudophenol halides (see above).

*o*-Isodurylene-quinone,  $\text{CH}_2:[1]\text{C}_6\text{H}(\text{CH}_3)_2[2]:\text{O}$ , m.p. 129°.

Tetrabromo-*o*-methylene-quinone,  $\text{CH}_2:[1]\text{C}_6\text{Br}_4[2]:\text{O}$ , m.p. about 130°.

Bromo-*o*-isodurylene-quinone,  $\text{CH}_2:[1]\text{C}_6\text{Br}(\text{CH}_3)_2[2]:\text{O}$ , m.p. 155°.

Dibromo-dimethyl-*o*-methylene-quinone,  $\text{CH}_2:[1]\text{C}_6\text{Br}_2(\text{CH}_3)_2:\text{O}$ , m.p. 168°.

Hexabromo-*p*-ethylidene-quinone,  $\text{CHBr}_2\text{CH}:[1]\text{C}_6\text{Br}_4[4]:\text{O}$ .

Tribromo-methoxy-*p*-propylidene-quinone,  $\text{CH}_3\text{CHBrCH}:[1]\text{C}_6\text{HBr}_2(\text{OCH}_3)_2[4]:\text{O}$ .

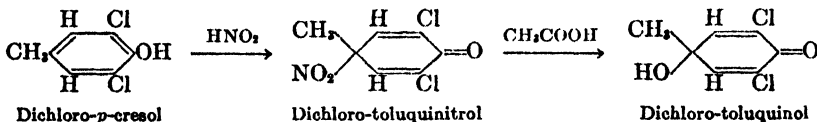
Hexabromo-*p*-*iso*-propylidene-quinone,  $\text{CH}_3(\text{CHBr}_2)\text{C}:[1]\text{C}_6\text{Br}_4[4]:\text{O}$ , m.p. 185°.

Much more stable methylene-quinones are known in the di- and triphenyl-methane series, e.g., *diphenyl-methylene-quinone*, or *quino-diphenylmethane*, and dyestuffs of the benzophenone, and triphenyl-carbinol groups, such as *auramine*, *rosaniline*, *rosolic acid*, etc., which may also be regarded as derived from methylene-quinone.

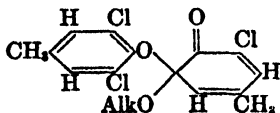
*Literature.*—*Auwers*, Ann. 301, 203; 334, 264; 344, 93; Ber. 32, 2978; 34, 4256; 36, 1878; 39, 3160; 44, 588, 788; *Zincke*, Ann. 320, 145; 322, 174; 329, 1; 349, 67; 350, 269; 353, 357; 381, 28.

**QUINOLS.** The quinols form a group of substances closely related to the pseudophenols and methylene-quinones on the one hand, and to the true quinones on the other (p. 233).

They were first obtained (1) by oxidising bromo- or chloro-*p*-alkyl-phenols with nitric acid, or oxides of nitrogen, when *nitroketones*, or *quinitrols*, are intermediate products:



*Bamberger* (Ber. 36, 2028) succeeded in obtaining quinols even from unhalogenated *p*-alkyl-phenols by using permonosulphuric acid as an oxidising agent, though the yield was small. When dichloro-toluquinitrol is boiled with methyl or ethyl alcohol it gives the ethers:





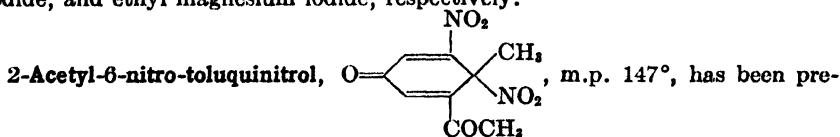
When submitted to the same treatment, quinol ethers undergo rearrangements in two directions. When heated with alcoholic sulphuric acid, both hydroquinone ethers and resorcinol ethers are formed, the latter arising from a migration of the alkoxy-group.

When halogenated methyl-quinols are heated with concentrated sulphuric acid, formaldehyde is split off, and *p,p'*-dihydroxyphenyl-methanes are formed. The isomeric *p*-hydroxy-benzyl alcohols, and their derivatives, the pseudo-phenol bromides, behave similarly, probably with intermediate formation of methylene quinones (Auwers, Ann. 356, 124). Tetrabromo-ethyl-quinol gives tribromo-ethyl-quinone when treated with concentrated sulphuric acid (Zincke, Ann. 341, 362).

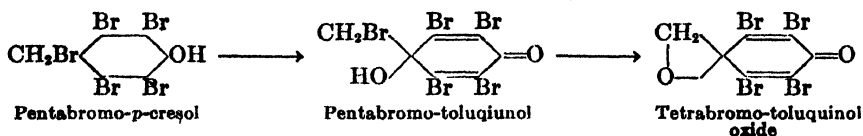
In halogenated quinols, one halogen atom, that occupying the *o*-position to the quinol group, is readily replaced by OH,  $\text{NHC}_6\text{H}_5$ , etc. Cf. the similar behaviour chloranils (p. 238).

Nitrochloro-*p*-cresol does not yield a quinol when heated with nitric acid, as would be expected, but nitrochloro-toluquinone, is formed instead; this is due to a rearrangement of the quinol to a hydroquinone, and subsequent oxidation. Nitrobromo- and nitro-dibromo-*p*-cresols behave similarly (Zincke, Ann. 341, 362). This atomic migration may take a different course according to the structure of the quinol (Auwers, Ber. 35, 443).

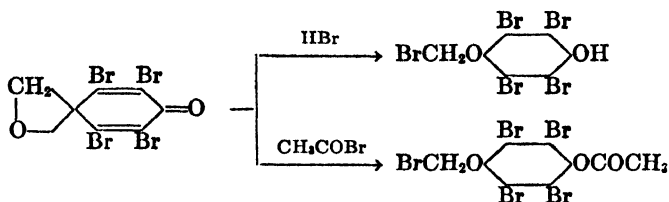
*p*-Toluquinol,  $\text{CH}_3(\text{OH})[4]\text{C}_6\text{H}_4\text{O}$ , m.p.  $75^\circ$ , has been obtained by the action of dilute sulphuric acid on *p*-tolyl-hydroxylamine, and in small quantities by the action of permonosulphuric acid on *p*-cresol. 2,4-Dimethyl-quinol,  $\text{CH}_3(\text{OH})[4]\text{C}_6\text{H}_3[2]\text{CH}_3\text{O}$ , m.p.  $73^\circ$ , is obtained by the action of cold, dilute sulphuric acid on *m*-xylyl- $\beta$ -hydroxylamine; when heated with acids, or alkalis, or when exposed to light, it gives *p*-xylo-hydroquinone (see above). 2,4-Dimethyl-quinol ethyl ether,  $\text{CH}_3(\text{OC}_2\text{H}_5)[4]\text{C}_6\text{H}_3[2](\text{CH}_3)\text{O}$ , b.p.  $94^\circ$  (12 mm.). Imino-2,4-dimethyl-quinol ethyl ether,  $\text{CH}_3(\text{OC}_2\text{H}_5)[4]\text{C}_6\text{H}_3[2](\text{CH}_3):\text{NH}$ , b.p.  $98^\circ$  (11 mm.), is prepared by the action of alcoholic sulphuric acid on *m*-xylyl- $\beta$ -hydroxylamine. Mesityl-quinol,  $\text{CH}_3(\text{OH})[4]\text{C}_6\text{H}_2[2,6](\text{CH}_3)_2\text{O}$ , m.p.  $46^\circ$ , is obtained from mesityl-hydroxylamine, and gives cumo-hydroquinone on rearrangement. 2,4,5-Trimethyl-quinol, m.p.  $116^\circ$ , is obtained by the action of permonosulphuric acid on pseudo-cumenol, and by the action of methyl magnesium iodide on *p*-xyloquinone (Bamberger, Ber. 36, 2038). Di-, tri-, and tetrachloro-toluquinols, m.p.  $123^\circ$ ,  $90^\circ$ , and  $166^\circ$ , respectively, are prepared from di-, tri-, and tetra-chloro-cresols by the action of nitric acid, either directly, or by the intermediate formation of the quintitrols (method 1). Di-, tri-, and tetra-bromo-toluquinols, m.p.  $134^\circ$ ,  $128^\circ$ , and  $205^\circ$ , respectively. When acted upon by alcoholic hydrogen chloride, chlorine replaces two bromine atoms of tetra-bromo-toluquinol, and one of tribromo-toluquinol, with the formation of dibromodichloro-toluquinol, m.p.  $162^\circ$ , and dibromo-chloro-toluquinol, m.p.  $135^\circ$ , respectively. Tetrabromo-ethyl-quinol,  $\text{C}_2\text{H}_5(\text{OH})[4]\text{C}_6\text{Br}_4\text{O}$ , m.p.  $140^\circ$ ; tetrabromo-methyl-ethyl-diquinol,  $\text{CH}_3(\text{OH})[1]\text{C}_6\text{Br}_4[4](\text{OH})\text{C}_2\text{H}_5$ , m.p.  $191^\circ$ , and tetrabromo-diethyl-diquinol,  $\text{C}_2\text{H}_5(\text{OH})[1]\text{C}_6\text{Br}_4[4](\text{OH})\text{C}_2\text{H}_5$ , m.p.  $180^\circ$ , are obtained from tetrabromo-ethyl-quinol by the action of methyl magnesium iodide, and ethyl magnesium iodide, respectively.



Nitric acid also oxidises pseudophenol bromides to quinols, which, when treated with alkalis, or silver oxide, lose hydrobromic acid, and give oxides:



These oxides add on hydrogen bromide and acetyl bromide to form derivatives of hydroquinone:



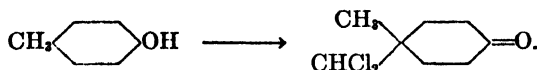
*Literature.*—Auwers, Ber. 35, 425, 443; Bamberger, Ber. 33, 3600; 35, 1424, 3886; 36, 1625; 40, 1890, 2236; Zincke, Ber. 34, 253; Ann. 328, 261; 341, 309; 343, 100.

## 2. Aromatic Hydroxy-monoaldehydes. Phenol Aldehydes

The phenol aldehydes can be obtained: (1) by oxidation of the phenol alcohols with chromic acid; (2) from the ozonides of propenyl phenols, the hydroxyl group being protected if necessary; (3) by an important synthetic process, in which chloroform and alkali act upon phenols. The chloroform provides the aldehyde group, which is in the *o*- or *p*-position to the phenolic hydroxyl (Reimer's reaction, 1876; Ber. 9, 1268):

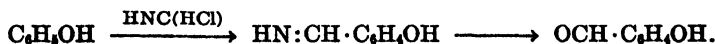


When *o*- and *p*-alkylated phenols are treated with chloroform and alkali, they yield partly phenol aldehydes, and partly chlorinated products, insoluble in alkali, and ketonic in nature, *e.g.*:



These substances are derivatives of keto-dihydrobenzene, and are therefore considered in connection with these compounds (Vol. II, p. 118). Chloral can be used in some of these reactions in place of chloroform. Hodgson (J. 1929, 1639) has investigated the proportions of *o*- and *p*-hydroxyaldehydes formed in Reimer's reaction, using chloroform and bromoform.

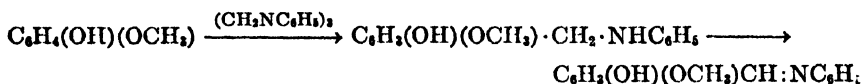
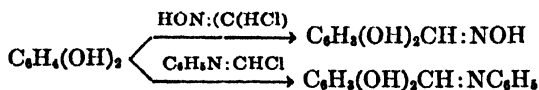
(4) Another important synthetic method of preparing the phenol aldehydes is the action of hydrocyanic acid and gaseous hydrogen chloride on phenols, or their ethers, with or without the addition of aluminium chloride (Gattermann, Ann. 357, 313). Aldimines are first produced, and they are readily converted into aldehydes:



With phenols, but not with the ethers, zinc cyanide can be substituted for hydrocyanic acid (Adams, Am. 45, 2373; 46, 1518). For by-products of the reaction, see Bell, J. 1928, 2215.

By similar reactions, (4a) oximes of phenol aldehydes are obtained by the action of mercury fulminate and hydrogen chloride on polyhydric phenols; (4b) phenylimines of phenol aldehydes are formed by the action of formanilide and phosphorus oxychloride on polyhydric phenols (Scholl, Ber. 34, 1441; Dimroth, Ber. 35, 993); and (4c) phenol ethers and anhydro-formaldehyde-aniline give hydroxy-benzyl-anilines, which can be dehydrogenated with nitrobenzene and caustic potash to hydroxy-benzanilines and further to hydroxyaldehydes:





(5) Hydroxy-aldehydes have been obtained by heating phenols with formaldehyde, or with ethers or esters of the hypothetical methylene-glycol, such as methylal- and methylene chloride, in the presence of an aromatic nitroso-compound, such as nitrosophenol, or nitrosonaphthol, and a catalyst, such as CuO, in methyl alcohol saturated with hydrogen chloride (Fr. Pat. 546,570; Br. Pat. 294,889; C. 1931, I, 1361).

(6) Resorcinol and other polyhydric phenols react with cyanogen bromide and hydrogen chloride with the formation of phenol-aldehydo-chloroimines, which are hydrolysed to phenol aldehydes:  $\text{C}_6\text{H}_4(\text{OH})_2 \longrightarrow \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CH}:\text{NCl} \longrightarrow \text{C}_6\text{H}_2(\text{OH})_2\text{CHO}$  (Karrer, *Helv.* 2, 89),

**Reactions.**—The reactions of the aldehyde group in phenol aldehydes are the same as in the ordinary aromatic aldehydes, such as benzaldehyde. They are oxidised only with difficulty to phenol carboxylic acids (see p. 185). They reduce ammoniacal silver nitrate, but not Fehling's solution. The best oxidising agent for converting them into carboxylic acids is fused caustic potash, to which lead dioxide may be added with advantage. *o*- and *p*-Hydroxy-aldehydes are oxidised by caustic potash at a moderate temperature, but *m*-hydroxy-aldehydes, when treated in the same way, undergo a Cannizzaro reaction with the simultaneous formation of an acid and an alcohol. The same occurs with the methyl ethers of *o*- and *p*-hydroxy-aldehydes (Lock, *Ber.* 61, 2234; 62, 1177). For the action of iodine and aqueous potash on hydroxy-aldehydes, see Windhaus, *Ber.* 56, 846. Dilute alkaline hydrogen peroxide readily oxidises the *o*- and *p*-phenol aldehydes to pyrocatechol and hydroquinone, respectively, the aldehyde group being split off (Dakin, *Am. Ch. J.* 42, 477). They are catalytically reduced to phenols in the presence of palladium; thus, salicylaldehyde gives *o*-cresol (Windaus, *loc. cit.*). The phenol aldehydes form two series of salts: colourless salts, with the normal formula,  $\text{CHO} \cdot \text{C}_6\text{H}_4\text{OK}$ , and coloured salts, usually yellow, with the quinoid formula  $\text{O}:\text{C}_6\text{H}_4:\text{C}(\text{H})\text{OK}$  (Hantzsch, *Ber.* 48, 1332). The salts give alkyl ethers with alkyl iodides or dialkyl sulphates. For the condensation of hydroxy-aldehydes with methyl-alkyl ketones see Iwamoto, *Bull. Japan*, 2, 51; Levy, *C.r.* 185, 133.

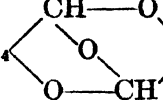
In salicylaldehyde, the phenolic hydrogen atom is linked to the oxygen of the CHO group by a coordinate linkage (*cf.* Sidgwick, *Electronic Theory of Valency*, p. 233).

#### (a) Monohydroxy-benzaldehydes, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$

The three isomerides required by theory are known. The first to be discovered was the methyl ether of *p*-hydroxy-benzaldehyde, known as anisaldehyde.

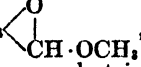
**Salicylaldehyde, *o*-hydroxybenzaldehyde**, m.p. 1.6°, b.p. 196°,  $d_{15}$  1.169, occurs in the essential oil of various species of *Spiraea*, *e.g.*,

*Spiraea ulmaria*. It was discovered by Piria in 1839, as an oxidation product of saligenin. It is obtained from *helicin*, the oxidation product of *salicin* (*q.v.*), by decomposition, and from sodium salicylate by reduction in the presence of boric acid (*Weil*, Ber. 41, 4147; U. S. Pat. 1,427,400), or electrolytically (*Mettler*, Ber. 41, 4148; *Rutovski*, Pharm. Moskva, 1928). The most convenient method of preparation is the Reimer-Tiemann process—the action of chloroform and alkali on phenol. Both salicylaldehyde and *p*-hydroxy-benzaldehyde are formed in this reaction. They are separated by steam distillation, the former being the more volatile. Industrially, *o*-cresol carbonate or other inorganic esters of *o*-cresol are chlorinated to the  $\text{CHCl}_2$  stage, and are then hydrolysed (Ger. Pat. 268,786), or *o*-cresol-aryl-sulphonic esters are oxidised with manganese dioxide and sulphuric acid. It is fairly soluble in water, and the solution gives a deep purple colour with ferric chloride (*cf.* saligenin, p. 335, and salicylic acid, p. 355). Its solution in alkali is intensely yellow, unlike that of the para-isomer (*Hantzsch*, Ber. 39, 3087). A solution of salicyl-

aldehyde dimerises at once to  $\text{C}_6\text{H}_4$    $\text{C}_6\text{H}_4$ , m.p. 130°,

under the influence of one drop of mineral acid, (*Adams*, Am. 44, 1126). Salicylaldehyde and benzaldehyde condense in the presence of sulphuric acid, to form a derivative of triphenylmethane,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5[\text{OH}]\text{CHO})_2$ , m.p. 55° (*Giacalone*, Gazz. 61, 301). A solution of salicylaldehyde in concentrated sulphuric acid is used as a reagent for detecting the rancidity of fats due to formation of ketones. Like all *o*-hydroxy-aldehydes it stains the skin a deep-yellow. On reduction it gives saligenin, and on oxidation, salicylic acid.

The potassium salt of salicylaldehyde,  $\text{KO}\cdot\text{C}_6\text{H}_4\cdot\text{CHO} + \text{H}_2\text{O}$ , forms yellow plates. The methyl ether,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CHO}$ , m.p. 38°, b.p. 238°; the anil of *o*-methoxy-benzaldehyde,  $\text{C}_6\text{H}_5(\text{OCH}_3)\text{CH}:\text{NC}_6\text{H}_5$ , b.p. 236° (30 mm.), decomposes into salicylaldehyde and methyl-aniline on heating with methyl iodide (*Freund*, Ber. 36, 1537). Ethyl ether, b.p. 248°. The dimethyl-acetal of salicylaldehyde loses methyl alcohol on heating to 130° *in vacuo* (0.5–1 mm.) forming the methyl-

lactolide,  $\text{C}_6\text{H}_4$  , m.p. 217–218°, the molecular weight of which is

doubled in benzene, but is simple in phenol, and in the gaseous state. Ethyl lactolide, m.p. 156° (*Bergmann*, Ann. 452, 135). Salicylaldehyde acetate,  $\text{CH}_3\cdot\text{COO}\cdot\text{C}_6\text{H}_4\text{CHO}$ , m.p. 38°, b.p. 253°, is formed from the aldehyde dissolved in acetic anhydride, in the presence of anhydrous potassium carbonate (*Schorygin*, Zhurnal, 3, 1189). Carbonate,  $(\text{CHOC}_6\text{H}_4)_2\text{CO}_2$ , m.p. 89° (*Einhorn*, Ber. 38, 3631). Glucoside, see *helicin*. *o*-Aldehyde-phenoxy-carbonic ester,  $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{COOC}_2\text{H}_5$ , b.p. 197° (90 mm.) (*Cajar*, Ber. 31, 2804). *o*-Aldehyde-phenoxy-acetic acid,  $\text{COOH}\cdot\text{CH}_2\text{O}[2]\text{C}_6\text{H}_4[1]\text{CHO}$ , m.p. 132°, gives *cumarilic acid*, on dehydration. Salicyl-aldoxime, m.p. 57° (see *Goldschmidt*, Ber. 22, 3102). This compound forms a characteristic copper salt, like the oximes of some other *o*-hydroxy-aldehydes (*Feigl*, Ber. 64, 2819). *o*-Anis-aldoxime,  $\text{CH}_3\text{O}[2]\text{C}_6\text{H}_4[1]\text{CH}:\text{NOH}$ , m.p. 92°, is obtained, together with *p*-anis-aldoxime, from anisole, by the action of mercury fulminate and hydrated aluminium chloride (*Goldschmidt*, Ber. 23, 2741; *Scholl*, Ber. 36, 648). Salicyl hydramide,  $(\text{C}_6\text{H}_5\text{O})_2\text{N}_2$ , m.p. 167° (*C*. 1899, II, 827; 1900, I, 123). Salicyl-hydrazone,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{NNH}_2$ , m.p. 96°; *o*-hydroxy-benzalazine,  $\text{HOC}_6\text{H}_4\text{CH}:\text{N}:\text{N}:\text{C}_6\text{H}_4\text{OH}$ , m.p. 213° (*Cajar*, Ber. 31, 2806), forms three physical isomers with

identical m.p.'s (Lockemann, Ber. 46, 1013). Phenylhydrazone, m.p. 142°, b.p. 234° (28 mm.), decomposes to some extent when boiled under ordinary pressures to aniline and salicylic nitrile,  $C_6H_4(OH)CN$  (Anselmino, Ber. 36, 580). For nitrosalicylaldehydes see Tiemann, Ber. 22, 2339.

*m*-Hydroxy-benzaldehyde, m.p. 104°, b.p. 240°, has been prepared by reducing *m*-hydroxybenzoic acid with sodium amalgam (Tiemann, Ber. 14, 969), and from *m*-nitro-benzaldehyde (Tiemann, Ber. 15, 2045). It condenses with aceto-bromo-glucose in alkaline solution to form tetra-acetyl-gluco-*m*-benzaldehyde, m.p. 108–109°, from which, by hydrolysis with ammonia, gluco-*m*-benzaldehyde,  $C_{12}H_{16}O_7$ , m.p. 160–161°, is obtained (Mauthner, J. pr. 129, 278). Oxime, m.p. 87°; phenylhydrazone, m.p. 130° (Ber. 24, 826). For nitro-*m*-methoxy-benzaldehydes, and bromo-derivatives, see Hodgson, J. 1931, 1500; Ulrich, Ber. 18, 2572.

*p*-Hydroxy-benzaldehyde, m.p. 116°, with sublimation, is obtained together with salicylaldehyde by the action of aqueous alkali on phenol and chloroform. It is also obtained by the action of hydrocyanic acid and hydrogen chloride on phenol (p. 343), or from *p*-amino-benzaldehyde (Walther, J. pr. 57, 535). Oxime, m.p. 65°; phenylhydrazone, m.p. 178°. For its halogen substitution products see Paal, Ber. 29, 2302; Auwers, Ber. 29, 2355. Its methyl ether is the readily accessible

Anisaldehyde, *p*-methoxybenzaldehyde,  $CH_3O[C_6H_4]CHO$ , b.p. 248°,  $d_{15}$  1.128, occurs in vanilla from Tahiti, in oil of Cassia, and other essential oils, and is found in old anise and fennel oil, and other oils, originally containing anethole, from which it is formed by oxidation. It can be prepared from anethole by the action of nitric acid, chromic acid, ozone, etc., or from *p*-cresol methyl ether by oxidation with permanganate and sulphuric acid, or electrochemically (Shorigyn, Zhurnal, 3, 1189; Fichter, Helv. 8, 332).

*p*-Anisaldoxime, m.p. 61°, and *p*-ethoxy-benzaldoxime,  $(C_2H_5O)[C_6H_4]CH:NOH$ , two modifications, m.p. 118° and 157°, have been prepared from anisole and phenetole, respectively, by the action of mercury fulminate and hydrated aluminium chloride. In the first case *p*-anisic nitrile and *o*-anisaldoxime are by-products (Scholl, Ber. 36, 648, 650). Anisal chloride,  $CH_3O \cdot C_6H_4 \cdot CHCl_2$ , m.p. 20° (Schmidt, Ber. 41, 2331).

2-Chloro-4-hydroxy-benzaldehyde, m.p. 147–148°, and 4-chloro-2-hydroxy-benzaldehyde, m.p. 52.5°, are formed from *m*-chlorophenol by Reimer's reaction (Hodgson, J. 1927, 1740).

*o*- and *p*-Mercapto-benzaldehydes, mobile oils which polymerise rapidly, are obtained from the amino-aldehydes, through the thiocyno-aldehydes with subsequent treatment with sodium sulphide. Phenylhydrazones, m.p. 127–129° and 136° (Friedländer, Ber. 45, 2083).

**HOMOLOGUES OF MONOHYDROXY-BENZALDEHYDES.** These have been prepared from various phenols by the methods of Reimer and Gattermann (p. 343):

*o*-Homosalicylaldehyde,  $CH_3[3]C_6H_4[2]OH[1]CHO$ , m.p. 17°, b.p. 208°.<sup>a</sup>

$\alpha$ -*m*-Homosalicylaldehyde,  $CH_3[4]C_6H_5[2]OH[1]CHO$ , m.p. 61°, b.p. 222°.<sup>a</sup>

$\beta$ -*m*-Homosalicylaldehyde,  $CH_3[6]C_6H_5[2]OH[1]CHO$ , m.p. 32°, b.p. 229°.<sup>b</sup>

*p*-Homosalicylaldehyde,  $CH_3[5]C_6H_5[2]OH[1]CHO$ , m.p. 56°, b.p. 217°.

*m*-Homo-*p*-hydroxybenzaldehyde,  $CH_3[3]C_6H_4[4]OH[1]CHO$ , m.p. 118°.<sup>c</sup>

*o*-Homo-*p*-hydroxybenzaldehyde,  $CH_3[2]C_6H_4[4]OH[1]CHO$ , m.p., 110°.

Trimethylsalicylaldehyde,  $(CH_3)_3[3,5,6]C_6H[2]OH[1]CHO$ , 105°.<sup>d</sup>

*p*-Thymotinaldehyde,  $(CH_3)_2[2]C_6H_7[5]C_6H_4[4]OH[1]CHO$ , m.p. 133°.<sup>e</sup>

*p*-Carvacrotinaldehyde,  $CH_3[5]C_6H_7[2]C_6H_5[4]OH[1]CHO$ , m.p. liquid.<sup>f</sup>

*p*-Isobutylsalicylaldehyde,  $C_4H_9[4]C_6H_5[2]OH[1]CHO$ , m.p. liquid, b.p. 252°.<sup>g</sup>

<sup>a</sup> Paschen, Ber. 24, 3667. <sup>b</sup> Chuit, Bull. [3], 35, 129. Anselmino, Ber. 50, 395.

<sup>c</sup> Gattermann, Ber. 31, 1766. <sup>d</sup> Auwers, Ber. 18, 2656; 32, 3598. <sup>e</sup> Kobek, Ber. 16, 2097; Gattermann, Ber. 31, 1767. <sup>f</sup> Lustig, Ber. 19, 14. <sup>g</sup> Dains, Am. J. 16, 434.

**p-Hydroxy-mesitylene-aldehyde**,  $(\text{CH}_3)_2[3,5](\text{OH})[4]\text{C}_6\text{H}_2\text{CHO}$ , m.p.  $114^\circ$ , is obtained from mesitol (p. 189) by oxidation with ethyl nitrite; *oxime*, m.p.  $169^\circ$  (Thiele, Ann. 311, 363).

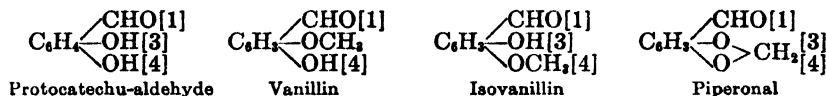
*o*-Hydroxy-benzaldehydes are more soluble in water, but less soluble in chloroform than the *p*-hydroxy-benzaldehydes. They are volatile with steam, and give difficultly soluble sodium bisulphite compounds; they give a yellow colour with ammonia. Rather unexpectedly, the phenylhydrazones of homosalicylaldehydes and other ring-alkylated salicylaldehydes are insoluble in alkali (Anselmino, Ber. 35, 4099).

***o*-Hydroxy-phenyl-acetaldehyde**,  $\text{HO}[2]\text{C}_6\text{H}_4\text{CH}_2\text{CHO}$ , b.p.  $90^\circ$  ("0" mm.), is obtained by ozonisation of *o*-allyl-phenol (Rinkes, Rec. 45, 819). ***p*-Methoxy-phenyl-acetaldehyde**, *homoisaldehyde*,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_4\text{CH}_2\text{CHO}$ , b.p.  $78-79^\circ$  (1.5 mm.), is obtained by ozonisation of chavicol-methyl ether (p. 450), and its *oxime*, m.p.  $120^\circ$ , by reduction of anisylidene-nitromethane,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}:\text{CHNO}_2$  (Harriss, Ber. 49, 1029; Bouveault, C.r. 135, 41).

***p*-Methoxy-hydrotopaldehyde**,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_3\text{CH}(\text{CH}_3)\text{CHO}$ , b.p.  $256^\circ$ , is obtained from anethole,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}:\text{CHCH}_3$ , by oxidation with mercuric oxide and iodine. A migration of the aromatic residue occurs (Bouveault, Ann. chim. phys. [7], 25, 483). It has been resolved into its optical antipodes,  $\alpha_D = +2.52^\circ$  and  $-2.45^\circ$  (Betti, Ber. 63, 874).

### (b) Dihydroxy-benzaldehydes

Dihydroxy-benzaldehydes can be obtained from dihydroxy-benzenes by nuclear synthesis with chloroform and alkali, or with hydrocyanic acid and hydrogen chloride, *etc.* (p. 343). Certain ethers derived from protocatechu-aldehyde possess a very pleasant odour, particularly *vanillin* and *piperonal*, both of which are manufactured on the large scale.

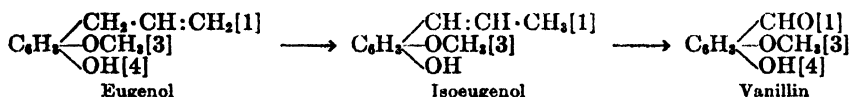


**Protocatechu-aldehyde**, 3,4-dihydroxy-benzaldehyde, m.p.  $153^\circ$  (Wegscheider, Mo. 14, 382), was discovered by Fittig and Remsen in 1871, who obtained it from piperonal (see below) (cf. Ger. Pat. 278,778). It can be prepared by heating vanillin, isovanillin or opianic acid (p. 381) with hydrochloric acid, and by oxidising *m*- or *p*-hydroxy-benzaldehyde with hydrogen peroxide in the presence of ferric salts (Ger. Pat. 155,731). When piperonal is heated with aluminium chloride in nitrobenzene solution, protocatechu-aldehyde is formed in good yield (Ger. Pat. 591,888). It is obtained synthetically by the action of chloroform and aqueous alkali on pyrocatechol. It dissolves readily in water, and the solution gives a deep-green colour with ferric chloride (p. 219). It reduces ammoniacal silver nitrate solution. When fused with potash it is converted into protocatechuic acid. Its two OH groups differ in reactivity (Pauly, Ann. 383, 288). Its phenylhydrazone occurs in two modifications:  $\alpha$ -(stable), m.p.  $176^\circ$ , and  $\beta$ -(unstable), m.p.  $121-128^\circ$ . *Oxime*, m.p.  $157^\circ$  (Wegscheider, Mo. 17, 245). **Protocatechu-aldehyde carbonate**,  $(\text{CO})\text{O}_2:\text{C}_6\text{H}_3\text{CHO}$  (p. 349), m.p.  $124^\circ$ , b.p.  $162^\circ$  (13 mm.). ***o*-Protocatechu-aldehyde**,  $(\text{HO})_2[2,3]\text{C}_6\text{H}_3\text{CHO}$ , m.p.  $105^\circ$ , has been prepared by Pauly (Ann. 383, 313) by demethylation of *o*-vanillin.

**Vanillin**, *m*-methoxy-*p*-hydroxy-benzaldehyde, m.p.  $83^\circ$ , sublimes readily. It is the active principle of the fruit of *Vanilla planifolia* (the ordinary vanilla pod), which contains about 2% of it. It is found in the orchids *Nigritella suaveolens* and *Gymnadenia albida*, in balsam of Peru, and other oils. It is found in small amounts in many other substances of vegetable origin, such as potato skins and blossoms, in the fresh bark of lime and beech, in some resins,

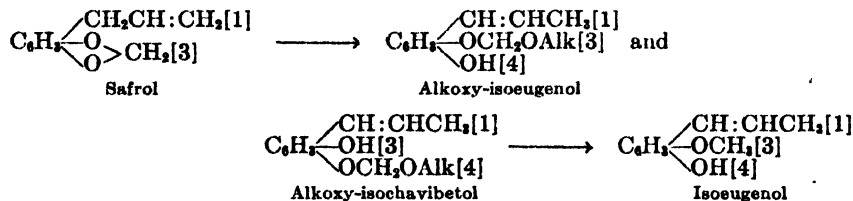
*etc.* In these cases the quantities present are so small that they can only be detected by the smell of vanillin. The waste liquor from the treatment of cellulose with sulphite contains 0.1 to 2.4 grams per litre of it. Here it is probably formed from the lignin of the wood (*Kurschner*, J. pr. 118, 238; *Honig*, *Angew.* 44, 845). It can be obtained from material containing lignin, such as straw, moss, wood, *etc.*, by mild ozonisation, or treatment with activated oxygen, potassium permanganate, *etc.* (Br. Pat. 319,747). *Tiemann* and *Haarmann* (1874) were the first to prepare it artificially by oxidising the glucoside, coniferin, with chromic acid. In this reaction glucovanillin can be isolated as an intermediate product. It is decomposed into glucose and vanillin by acids or emulsin (*Tiemann*, *Ber.* 7, 613; 9, 1287; 14, 2023; 18, 1595, 1657). When protocatechu-aldehyde is methylated by means of dimethyl sulphate, vanillin is formed, together with much isovanillin (see below) (Ger. Pat. 122,851). It is synthesised from guaiacol, which is treated with chloroform and caustic potash, or with hydrocyanic acid and hydrogen chloride. In the former case, *m*-methoxy-salicylaldehyde, *o*-vanillin, m.p. 45°, b.p. 266°, is formed simultaneously (*Noelting*, *Ann. ch. ph.* [8], 19, 476).

Vanillin is manufactured on the large scale from *eugenol*, which can be readily obtained from clove oil. It is first converted into *isoeugenol*, and then oxidised. During oxidation, the free hydroxyl group must be protected by temporary esterification with acetic acid or phenyl sulphonic acid, or some similar acid.



The oxidising agents used are potassium dichromate and sulphuric acid, with the addition of some sulphanilic or anthranilic acid (Sw. Pats. 89,053 and 91,088), ozone (*Will*, *Ber.* 48, 232; *Briner*, *Helv.* 7, 62), nitrobenzene and caustic potash (Br. Pats. 285,156 and 290,649). The oxidation may also be effected electrochemically (*Fichter*, *Helv.* 8, 394).

Another process starts from *safrol* (p. 452), from which two isomeric phenols are obtained by fission of the  $\text{CH}_2\text{O}_2$  group; these are methylated, and the  $\text{CH}_2 \cdot \text{OAlk}$  group is removed; or the hydroxyl is temporarily esterified, and the order of the two reactions is reversed. In both cases, isoeugenol results:



Reactions (4) and (5) mentioned on p. 343 indicate many methods by which guaiacol can be converted into vanillin, and some of these are used industrially (*Wagner*, *Chem. Ztg.* 52, 379; *Schwyzer*, *Chem. Ztg.* 54, 817, 839).

When heated with hydrochloric acid, vanillin is decomposed into protocatechu-aldehyde and chloroform. It behaves as a *p*-hydroxy-benzaldehyde (p. 346), and is converted into protocatechuic acid when fused with caustic potash. Its constitution follows from the above two reactions. It is reduced by sodium amalgam to vanillyl alcohol (p. 338) and *hydrovanillinol*, a compound correspond-

ing to hydrobenzoin (p. 267). **Vanillin-oxime**, m.p. 117° (Marcus, Ber. 24, 3654). **Trithiovanillin**,  $[C_6H_4(OH)(OCH_3)CSH]_3$ , m.p. 236° (Woerner, Ber. 29, 143). The 3-ethyl ether of protocatechu-aldehyde,  $C_6H_4[1]CHO[3]OC_2H_5[4]OH$ , m.p. 77.5°, which is obtained by ethylation of protocatechu-aldehyde, or by ethylation of the fission products of safrol, mentioned above, followed by further treatment, tastes and smells four times stronger than vanillin. It is made commercially, and marketed under the names *bourbonal*, *ethyl-vanillin*, *quadrivanil*, etc.

**Isovanillin**, *p-methoxy-m-hydroxy-benzaldehyde*, m.p. 116°, smells, when warm, of vanillin and anise-oil. It is obtained from protocatechu-aldehyde by methylation (p. 347), and by oxidation of *hesperitinic acid* (p. 476). It is also obtained by heating *opianic acid* (p. 381), with hydrochloric acid. **O-Methyl-vanillin**, *p-veratraldehyde*,  $(CH_3O)_2C_6H_3CHO$ , m.p. 43°, b.p. 283° (Tiemann, Ber. 11, 662); **O-ethyl-vanillin**, m.p. 65°. Both these compounds can be obtained by treating vanillin with the necessary dialkyl sulphate and sodium hydroxide (Hann, Ac. Washington, 24, 126). **Isobourbonal**, *safrovanillin*,  $HO[3]C_6H_3O[4]C_2H_5CHO$ , m.p. 126°; **ethyl-bourbonal**,  $(C_2H_5O)_2[3,4]C_6H_3CHO$ , m.p. 25° (Brit. Pats. 294,889 and 290,469). **3-Methoxy-4-hydroxyphenyl-acetaldehyde**, *homovanillin*,  $HO[4]CH_3O[3]C_6H_3CH_2CHO$ , m.p. 50.5°, has been prepared by Harries (Ber. 48, 868) by ozonising eugenol; its odour is not so marked as that of vanillin. Ring-methylated vanillins have been obtained from the three cresols by Reimer's reaction (Koetschet, Helv. 13, 474). **Homoveratraldehyde**,  $(CH_3O)_2C_6H_3CH_2CHO$ , b.p. 121° (0.35 mm.) is obtained by ozonising eugenol methyl ether (Harries, Ber. 49, 1020).

**Piperonal**, *heliotropin*,  $(CH_3O)_2C_6H_3CHO$ , m.p. 37°, b.p. 263°, has been obtained by oxidising piperic acid (p. 481), and by treating protocatechu-aldehyde with alkali and methylene iodide. It is manufactured commercially from safrol (p. 452) by a process similar to that by which vanillin is obtained from eugenol (see above). It has a very pleasant odour of heliotrope. It gives piperonic acid (p. 366) on oxidation, and piperonyl alcohol (p. 338) on reduction. When heated with dilute mineral acids to about 190° under pressure, it breaks down into protocatechu-aldehyde and formaldehyde, or methyl alcohol (Ger. Pat. 162,822). **Oxime**, m.p. 110°; *phenylhydrazone*, m.p. 100°; *diacetate*, m.p. 89-91° (Ger. Pat. 295,337). Phosphorus pentachloride in the cold converts it into **piperonal dichloride**,  $(CH_3O)_2C_6H_3CHCl_2$ , m.p. 59°, and on heating into **dichloro-piperonal dichloride**,  $(CCl_2O)_2C_6H_3CHCl_2$ , m.p. 15°, b.p. 153° (9 mm.). When the latter is acted upon by cold water it gives the **carbonate of protocatechu-aldehyde dichloride**,  $(CO)_2O_2C_6H_3CHCl_2$ , m.p. 97°, b.p. 178° (15 mm.), which is also obtained from piperonal itself by the action of thionyl chloride at 220°, or by heating with sulphur chloride. Anhydrous oxalic acid, formic acid, etc., convert it into protocatechu-aldehyde carbonate (p. 347). When acted upon by hot water it gives protocatechu-aldehyde. When reduced with zinc dust and glacial acetic acid, *homopyrocatechu-carbonate*,  $(CO)_2O_2C_6H_3CH_2$ , is formed (Ber. 42, 417). Diazomethane gives acetopiperone (p. 352), and *piperonyl-acetone* (p. 353) (Mosettig, Ber. 61, 1391); diazoethane reacts similarly (Mosettig, Mo. 57, 291). **Bromo-piperonal**,  $(CH_3O)_2C_6H_3BrCHO$  (Oelker, Ber. 24, 2592). **o-Nitro-piperonal**, m.p. 98.5° (Ekeley, Am. 50, 2711), gives bis-methylenedioxy-indigo (Liebermann, Haber, Ber. 23, 1566). **6-Aminopiperonal**, m.p. 107°, obtained by reducing nitropiperonal with temporary protection of the CHO-group, has been used for preparing 6-halogeno-piperonals by diazotisation and subsequent treatment by the Sandmeyer reaction (Rilliet, Helv. 4, 588). **Homopiperonal**,  $(CH_3O)_2C_6H_3CH_2CHO$ , m.p. 69°, b.p. 144° (10 mm.), is obtained by ozonisation of safrol. It may also be obtained by oxidising safrol with potassium permanganate, when safrol-glycol is formed, and treating the latter with lead tetraacetate (Semmler, Ber. 41, 2751). Its *oxime*, m.p. 120°, is obtained by reducing piperonylidene-nitromethane with aluminium amalgam (Bouvalet, C.r. 135, 41), or by ozonising safrol, reducing the product catalytically, making the bisulphite compound, and acting on it with hydroxylamine hydrochloride (Hahn, Ber. 67, 1486).

For **nitro-protocatechu-aldehyde**, **halogeno-vanillins**, **nitro-vanillin**, **amino-vanillin**, and their derivatives, see Hayduck, Ber. 36, 2930; Raiford, Am. 52, 4576).

The following aldehydes are obtained by exactly similar reactions as those by

which protocatechu-aldehyde is obtained from pyrocatechol:  $\beta$ -Resorcyraldehyde,  $(\text{HO})_2[2,4]\text{C}_6\text{H}_3[1]\text{CHO}$ , m.p.  $135^\circ$ , from resorcinol, chloroform and alkali, or better with hydrocyanic acid and hydrogen chloride (Gattermann, Ber. 32, 279) of diphenyl-formamidine (Shoosmith, J. 123, 2704). It can also be obtained from the corresponding dihydroxy-benzoyl chloride, the OH-groups being temporarily protected (Mauthner, J. pr. 101, 93); cf. umbelliferone, p. 477. Orcyl-aldehyde,  $(\text{HO})_2[2,4]\text{C}_6\text{H}_3[6,1](\text{CH}_3)\text{CHO}$ , m.p.  $180^\circ$ , is made from oreinol, and gentisicaldehyde,  $(\text{HO})_2[2,5]\text{C}_6\text{H}_3[1]\text{CHO}$ , m.p.  $99^\circ$ , from hydroquinone by the action of chloroform and alkali. In dilute solution, dihydroxy-dialdehydes are formed if excess of chloroform and alkali is used. *p*-Orcyl-aldehyde, *atranol*,  $(\text{HO})_2[2,6]\text{C}_6\text{H}_3[4](\text{CH}_3)[1]\text{CHO}$ , m.p.  $124^\circ$ , is a degradation product of various lichen acids (Pfau, Helv. 9, 650; Schoepf, Ann. 491, 220). The monomethyl ethers of resorcinol and hydroquinone, like guaiacol, always give two aldehydes when treated with chloroform and caustic potash. One resembles salicylaldehyde, and has the aldehyde-group ortho to the phenol hydroxyl, and the other has the aldehyde-group para to the hydroxyl (Tiemann, Ber. 14, 204). Thus, resorcinol monomethyl ether gives rise to 2-hydroxy-methoxy-benzaldehyde m.p.  $41-42^\circ$  (found in the root of *Chlorocodon Wightii*) (Friedländer, Mo. 30, 879), and 4-hydroxy-methoxy-benzaldehyde, m.p.  $153^\circ$ , by method 4 (p. 343). These substances can be separated by steam distillation, the former being volatile in steam. Gentisicaldehyde has also been obtained by oxidising salicylaldehyde or *m*-hydroxy-benzaldehyde in alkaline solution with potassium persulphate (Neubauer, Z. physiol. Chem. 52, 355; Hodgson, J. 1927, 2339). The anil of resorcyraldehyde,  $\text{C}_6\text{H}_3[2,4](\text{OH})_2\text{CH}:\text{NC}_6\text{H}_5$ , m.p.  $126^\circ$ , is also obtained by the action of formanilide and phosphorus oxychloride on resorcinol, and the oxime,  $\text{C}_6\text{H}_3(\text{OH})_2\text{CH}:\text{NOH}$ , by the action of mercury fulminate and hydrochloric acid on resorcinol.

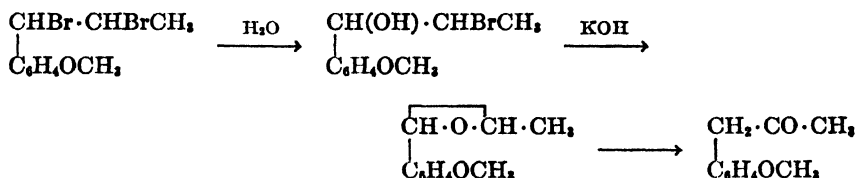
### (c) tri- and tetra-Hydroxy-benzaldehydes

Pyrogallol, phloroglucinol, and hydroxy-hydroquinone are converted into their corresponding aldehydes by the action of hydrocyanic acid and hydrogen chloride. Pyrogallaldehyde,  $(\text{HO})_3[2,3,4]\text{C}_6\text{H}_2\text{CHO}$ , m.p.  $161^\circ$ . Its trimethyl ether, m.p.  $37^\circ$ , b.p.  $170^\circ$  (12 mm.), is obtained by catalytic reduction of the corresponding acid chloride (Slotta, Ber. 63, 3029), and from pyrogallol-trimethyl ether by method 3 (Schaaf, Helv. 7, 357). 3,4,5-Pyrogallaldehyde, gallaldehyde, m.p.  $212^\circ$  (decomp.). Its 3-monomethyl ether, m.p.  $133^\circ$ , has been obtained from bromo-vanillin and alkali (Bradley, J. 1930, 793). Its 3,4-dimethyl ether, *iridicaldehyde*, m.p.  $60-61^\circ$  (Mauthner, Ann. 449, 102), and its trimethyl ether, m.p.  $74^\circ$ , have also been obtained from the corresponding acid chlorides (Slotta, J. pr. 133, 129). 5-Methoxy-3,4-methylene-dioxy-benzaldehyde, *myristicin aldehyde*, m.p.  $130^\circ$ , is prepared from isomyristicin (p. 454) by oxidation with permanganate, or from gallaldehyde-3-methyl ether by the action of methylene sulphate and alkali (Balzer, J. 1932, 1281). Phloroglucin-aldehyde,  $(\text{HO})_3[2,4,6]\text{C}_6\text{H}_2\cdot\text{CHO}$ , melts with decomposition. Hydroxy-hydroquinone-aldehyde,  $(\text{HO})_3[2,4,5]\text{C}_6\text{H}_2\cdot\text{CHO}$ , m.p.  $223^\circ$  (Gattermann, Ber. 32, 278). Some oximes and anils of these aldehydes have been prepared synthetically by methods 4a and 4b (p. 343). Certain aromatic compounds with unsaturated aliphatic side chains obtained from vegetable sources give alkyl- and methyl-ethers of tetrahydroxy-benzaldehydes on oxidation (Will, Ber. 16, 2112; 17, 1086; Semmler, Ber. 24, 3818; 41, 1918). Thus, glycosyring-aldehyde, an oxidation product of *syringin*, gives 4-hydroxy-3,5-dimethoxy-benzaldehyde, syringaldehyde, m.p.  $113^\circ$ , with emulsin. This compound has been synthesised from 1,3-pyrogallol-dimethyl ether (Pauly, Ber. 62, 2277), and from acetyl-syringic acid by method 2e (p. 264) (McCord, Am. 53, 4181). 2,4,5-Trimethoxy-benzaldehyde, *asaryl-aldehyde*, m.p.  $114^\circ$ , is obtained from *asarone*, propenyl-trimethoxy-benzene, by oxidation, and from hydroxyhydroquinone methyl ether by the action of hydrocyanic acid, hydrogen chloride, and aluminium chloride (Fabinyi, Ber. 39, 1211; Gattermann, Ber. 32, 289). When one drop of sulphuric acid is added to a solution of *asaryl-aldehyde* in acetic acid, the methoxy groups in the 2,5-positions are displaced, and a quinone,  $\text{CH}_3\text{O}[4](\text{O}:)[5]\text{C}_6\text{H}_3[2](\text{:O})\text{CH}(\text{OCOCH}_3)_2$ , m.p.  $145^\circ$ , is formed. 2,3,4,5-Tetrahydroxy-benzaldehyde, indefinite m.p.; 2,5-dimethoxy-3,4-methylene-dioxy-benzaldehyde, *apiol-aldehyde*, m.p.  $102^\circ$ , is obtained

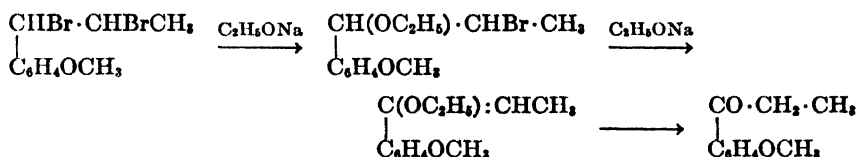
from parsley isoeuphonyl, and 5,6-dimethoxy-3,4-methylene-dioxy-benzaldehyde, dill-apiol-aldehyde, m.p. 75° from dill isoeuphonyl (*Thoms*, *Ar. Pharm.* [2], 42, 344; *Fabinyi*, *Ber.* 50, 1335).

### 3. Phenol Monoketones

Phenol-ketones have been obtained: (1a) from amino-ketones; (1b) from halogeno-ketones by hydrolysis under pressure in the presence of cuprous oxide (*U. S. Pat.* 1,961,630); (2) from aromatic  $\beta$ -keto-carboxylic acids (*Tahara*, *Ber.* 25, 1308); (3) by decomposing C-alkylated benzo-tetronic acids with concentrated alkalis (*Anschütz*, *Ann.* 379, 333); (4) from the dibromides of propenyl-phenols or their ethers (a) by converting them into bromohydrins and ethylene oxides, and bringing about a rearrangement of the latter either by means of acids, or by heating them alone (*Horing*, *Ber.* 38, 3464):



(b) by converting them into ethyl-bromohydrins and  $\alpha$ -ethoxy-propenyl phenols, followed by hydrolysis of the latter:



Nuclear-synthetic methods are known for the introduction of acid residues into phenols and phenol-alkyl ethers: (5) phenols may be condensed with acetic and other fatty acids by means of zinc chloride, stannic chloride, or better phosphorus oxychloride (*Nencki*, *Ber.* 14, 1566; *Ger. Pat.* 49,149); (6) phenols are acted upon by acid chlorides, preferably in the presence of zinc chloride (*Perkin*, *J.* 55, 546; *Eijkman*, *Weekbl.* 1, 453); (7) phenol-alkyl ethers, or phenols themselves, are acted upon by acid chlorides in the presence of aluminum chloride or stannic chloride (*Auwers*, *Ber.* 36, 3890; *Stadnikov*, *Ber.* 61, 1996; *Ger. Pat.* 15,901), preferably dissolved in nitrobenzene (*Rosenmund*, *Ar. Pharm.* 265, 308). This method has been used for the preparation of thiophenol-monoketones from thiophenol ethers (*Ger. Pat.* 203,083). (8) Phenols react with aliphatic nitriles in ether solution under the influence of zinc chloride and hydrogen chloride (*Hoesch*, *Ber.* 48, 1122; *Karrer*, *Helv.* 2, 466). (9) Aliphatic esters of (poly)-phenols rearrange when heated with aluminium chloride in nitrobenzene (*Rosenmund*, *Ber.* 61, 2801), or zinc chloride (*Rosenmund*, *Ann.* 460, 56; *Couthard*, *J.* 1830, 280), or ferric chloride (*Huber*, *Mo.* 56, 332), the acyl group changing from the hydroxy group over to the ring, in most cases entering the *o*-position to the hydroxyl (*Fries*, *Ber.* 41, 4271; *Wittig*, *Ber.* 57, 88). This "Fries" migration is regarded as a special case of the Friedel-Crafts reaction (*Auwers*, *Ann.* 460, 240; 464, 293). (10) Some alkoxy-phenyl ketones have been obtained from alkoxy-phenyl-carboxylic esters by condensation with sodium and ethyl acetate, followed by ketonic hydrolysis of the alkoxy-benzoyl-acetic esters first formed (*Mauthner*, *J. pr.* 112, 57), and (11) some alkoxy-phenyl methyl ketones have been obtained similarly from alkoxy-benzaldehydes and diazomethane (*Mosettig*, *Ber.* 61, 1391).

The *o*- and *p*-hydroxyphenyl-alkyl ketones are separated by steam distillation, the former being volatile in steam, like the *o*-hydroxy-aldehydes (p. 345). When reduced with amalgamated zinc and hydrochloric acid (Clemmensen's method) the hydroxy ketones are converted into alkyl-phenols. The *o*-hydroxy ketones with a free hydroxyl-group, like the *o*-hydroxy-aldehydes, form two series of salts,



normal colourless phenates,  $\text{CH}_3\text{COC}_6\text{H}_4\text{OM}$ , and coloured quinoid salts,  $\text{O}:\text{C}_6\text{H}_4:(\text{OM})\text{CH}_3$ .

*o*-Hydroxy-acetophenone, m.p.  $28^\circ$ , b.p.  $263^\circ$ , occurs in oil from the wood and bark of *Chione glabra* (Dunstan, J. 75, 66), and has been prepared by methods 2, 3, and 5 (Freudenberg, Ber. 55, 1748). *p*-Hydroxy-acetophenone, *piceol*, m.p.  $109^\circ$ , has been obtained from the glucoside *picein*, by hydrolysis, and by methods 1, 5, 6, and 9. For homologues, see Hill, Am. 37, 1839. *p*-Acetyl-anisole, *p*-methoxy-acetophenone, m.p.  $39^\circ$ , b.p.  $263^\circ$ , has a smell of hawthorn; it is obtained by method 7. Propionyl-phenol,  $\text{HOC}_6\text{H}_4\text{COC}_2\text{H}_5$ , m.p.  $148^\circ$ , is obtained by method 6. For butyryl, valeryl-, and the higher acyl-phenols of the *o*- and *p*-series, see Huber, Mo. 56, 322; Sandulesco, Bull. 47, 1300.

1,3,4-Aceto-pyrocatechol,  $(\text{HO})_2[3,4]\text{C}_6\text{H}_3[1]\text{COOH}$ , m.p.  $116^\circ$  (Dzierzgowski, Ber. 27, 1989). 1,2,3-Aceto-pyrocatechol, m.p.  $97-98^\circ$ , occurs in coffee oil (Schimmel's Ber. 1929, 52). Aceto-guaiacol, *acetvanillone*, *apocynin*,  $\text{HO}[4](\text{CH}_2\text{O})[3]\text{C}_6\text{H}_3[1]\text{COCH}_3$ , m.p.  $115-116^\circ$ , occurs as a glucoside, which is the chief constituent of Canadian hemp (*Apocynum cannabinum*), and other *Apocynana*. It is an oxidation product of aceto-eugenol, and has been obtained synthetically: from guaiacol by methods 7 and 9, from the corresponding carbinol (p. 338), and from benzoyl-vanillin by condensation with methyl magnesium iodide, followed by oxidation, and removal of the benzoyl group (Tiemann, Ber. 24, 2885; Otto, Ber. 24, 2869; Finemore, J. 93, 1513, 1520). It is a cardiac stimulant and a diuretic (Howells, Am. 52, 4076). Aceto-isovanillones, m.p.  $67-68^\circ$ , and  $91^\circ$  have been described by Schneider, Ber. 55, 1892, and Reichstein, Helv. 10, 392. 1,3,4-Aceto-veratrone,  $(\text{CH}_2\text{O})_2\text{C}_6\text{H}_3[1]\text{COCH}_3$ , m.p.  $48^\circ$  (Dzierzgowski, Ber. 27, 1989). 1,2,3-Aceto-veratrone,  $(\text{CH}_2\text{O})_2[2,3]\text{C}_6\text{H}_3[1]\text{COCH}_3$ , b.p.  $143-144^\circ$  (14 mm.), is prepared from *o*-veratrol-*o*-carboxylic ester by method 10 (Mauthner, J. pr. 112, 57). Aceto-piperone,  $(\text{CH}_2\text{O})_2[3,4]\text{C}_6\text{H}_3[1]\text{COCH}_3$ , m.p.  $87-88.5^\circ$ , is obtained from protocotoin by oxidation with permanganate (Ciamician, Ber. 24, 2989; 25, 1127; 26, 2348), or by method 10 (Mauthner, J. pr. 116, 321), or 11 (Moseltig, Ber. 61, 1391).

Resacetophenone,  $(\text{HO})_2[2,4]\text{C}_6\text{H}_3[1]\text{COCH}_3$ , m.p.  $142^\circ$ , is formed by methods 5 and 6 and from  $\beta$ -methyl-umbelliferone by fusion with potash (Pechmann, Ber. 16, 2123). For its derivatives, see Dahse, Ber. 41, 1619. Its *p*-methyl ether, paeonol,  $\text{CH}_3\text{O}[4](\text{HO})[2]\text{C}_6\text{H}_3\text{COCH}_3$ , m.p.  $52^\circ$ , occurs as a glucoside (the m.p. of the synthetically prepared glucoside is  $118^\circ$ ) in the root bark of *Paeonia Moutan*, a Japanese ranunculacea (Tahara, Ber. 25, 1292). It has been synthesised from resorcinol and acetyl chloride, with subsequent methylation. An isomeric resacetophenone, m.p.  $178^\circ$ , is obtained when resorcinol diethyl ether is acetylated in the presence of aluminium chloride, 1,2,4-resacetophenone diethyl ether, m.p.  $69^\circ$ , being formed at the same time (Claus, J. pr. 53, 39). For halogeno-derivatives of resacetophenone, see Segalle, Mo. 17, 314; for paeonol derivatives, see Shinoda, Pharm. Japan, 52, 91. The dimethyl ether, m.p.  $73^\circ$ , of 2,6-dihydroxy-acetophenone, m.p.  $157^\circ$ , is obtained from dimethoxy-benzonitrile by the action of methyl magnesium iodide, and gives 3,5-dihydroxy-acetophenone, m.p.  $147-148^\circ$ , with aluminium chloride (Mauthner, J. pr. 107, 103; 139, 290). Other ketones derived from resorcinol have been prepared by Karrer (Helv. 4, 707).

Orcacetophenone-dimethyl ether,  $\text{CH}_3[4]\text{C}_6\text{H}_3[2,6](\text{OCH}_3)_2[1]\text{COCH}_3$ , m.p.  $89^\circ$  and *iso*-orcacetophenone-dimethyl ether,  $\text{CH}_3[6]\text{C}_6\text{H}_3[2,4](\text{OCH}_3)_2[1]\text{COCH}_3$ , m.p.  $48^\circ$ , are obtained from orcinol-dimethyl ether by method 7 (Tambor, Ber. 41, 793).

Quinacetophenone,  $(\text{HO})_2[2,5]\text{C}_6\text{H}_3[1]\text{COCH}_3$ , m.p.  $202^\circ$ , is obtained by method 5, and by exposing a mixture of quinone and acetaldehyde to sunlight (p. 235). Valero-hydroquinone,  $(\text{HO})_2[2,5]\text{C}_6\text{H}_3\text{COC}_2\text{H}_5$ , m.p.  $115^\circ$ ; its quinhydrone (p. 237) is formed when quinone and valeraldehyde are exposed to sunlight (Klinger, Ber. 24, 1344). For other dimethoxy-phenyl alkyl ketones, see Majima, Ber. 55, 215.

*o*-Gallacetophenone,  $(\text{HO})_2[2,3,4]\text{C}_6\text{H}_3[1]\text{COCH}_3$ , m.p.  $168^\circ$ , is obtained by method 5. Its 3,4-dimethyl ether, m.p.  $83^\circ$ , is obtained from pyrogallol-trimethyl ether, acetyl chloride and aluminium chloride. (Nencki, Ber. 27, 2737; Fischer, Ber. 42, 1018; Barcellini, Gazz. 46, I, 249). 3,4,5-Trihydroxy-acetophenone, *p*-gallacetophenone,  $(\text{HO})_3[3,4,5]\text{C}_6\text{H}_2\text{COCH}_3$ , m.p.  $184-185^\circ$ , has been prepared from its trimethyl ether; and its 3,5-dimethyl ether, *acelosyringone*,

m.p. 122–123°, has been obtained from acetyl-pyrogallol-1,3-dimethyl ether by method 9 (*Mauthner*, J. pr. 115, 137; 121, 255). 2,4,6-Trihydroxy-acetophenone, *phloracetophenone*,  $(\text{HO})_3[2,4,6]\text{C}_6\text{H}_2\text{COCH}_3$ , m.p. 218° (anhydrous), is obtained by the partial hydrolysis of triacetophloroglucinol (*Heller*, Ber. 45, 423); its 2,4-dimethyl ether, m.p. 82–83°, occurs in various essential oils of the *Xanthoxylum* species. For its synthesis, see *Friedländer*, Ber. 30, 2152. For other phloracetophenone ethers, see *Sonn*, Ber. 58, 1691; 61, 2300; and for other hydroxyketones derived from phloroglucinol see *Karrer*, *Helv.* 2, 466; 3, 395; 4, 707; and Br. Pat. 157,854.

2,4,5-Trihydroxy-acetophenone,  $(\text{HO})_3[2,4,5]\text{C}_6\text{H}_2\text{COCH}_3$ , has been obtained in reddish-brown needles, m.p. 206°, by *Chadha* (J. 1933, 1073), by the action of zinc chloride and acetic acid, or acetonitrile on hydroxy-hydroquinone, and from hydroxy-hydroquinone triacetate by the action of aluminium chloride and nitrobenzene. It has also been obtained by the action of ferrous sulphate and potassium persulphate on resacetophenone (*Bargellini*, *Gazz.* 43, I, 164; *Lincei* 20, I, 32; cf. *Mauthner*, J. pr. 136, 204). 2,4,5-Trimethoxy-propiophenone, m.p. 106–108°.

Butyryl-methyl-phloroglucinol monomethyl ether, *aspidinol*  $\text{C}_6\text{H}_2\text{CO}[1]\text{CH}_2[3]\text{C}_6\text{H}[2,6](\text{OH})_2[4]\text{OCH}_3$ , m.p. 143°, see Vol. II, p. 400. 2,3,4,6-Tetramethoxy-acetophenone, m.p. 43–45°, is obtained from 1,2,3,5-tetramethoxybenzene by method 7 (*Bargellini*, *Lincei*, 19, II, 595).

p-Methoxy-phenylacetone, *anise-ketone*,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_4\text{CH}_2\text{COCH}_3$ , b.p. 263°, occurs in anise, and possibly in fennel oil (C. 1902, II, 1256), and is formed by a rearrangement of anethole oxide when heated (*Mannich*, Ber. 43, 189). Piperonyl-acetone,  $\text{CH}_3\text{O}_2[3,4]\text{C}_6\text{H}_3\text{CH}_2\text{COCH}_3$ , m.p. 55° (*Kaufmann*, Ber. 49, 675). δ-3,4-methylene-dioxyphenyl-butyl-methyl ketone,  $(\text{CH}_2\text{O}_2)\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COCH}_3$ , m.p. 28°, has been prepared by hydrogenating piperonylideneacetone (p. 461) (*Borsche*, Ber. 60, 984). β-(o-Hydroxyphenyl)-ethyl-ethyl ketone,  $\text{HO}[2]\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_3$ , m.p. 72° is obtained by the reduction of o-hydroxystyryl-ethyl ketone (*Murai*, *Tohoku Rep.* 17, 695).

4-Hydroxy-3-methoxy-benzylacetone, *zingerone*,  $\text{HO}[4]\text{CH}_2\text{O}[3]\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ , m.p. 41°, is, like *shogaol*, a degradation product of *zingerol* from ginger root; it has a burning taste. It has been synthesised by condensing vanillin with acetone, and reducing the resulting unsaturated ketone with sodium amalgam, or condensing with acetoacetic ester, reducing the product, and hydrolysing the resulting unsaturated ester, followed by ketolysis (Vol. II, p. 393). Zingerone-methyl ether, m.p. 55–56° is prepared from zingerone, or synthetically from veratraldehyde by a similar method to the synthesis of zingerone. When isovanillin is used in place of vanillin in the above synthesis, *isozingerone*, b.p. 159–160° (4 mm.) is obtained (*Nomura*, *Lapworth*, J. 111, 769, 777, 790; *Murai*, *Tohoku Rep.* 14, 145, 149). Homologues of zingerone have been prepared by *Pearson*, *Pharm. J.* 49, 78, *Murai*, *loc. cit.*, and *Nomura*, *Tohoku Rep.* 16, 589.

o-Acetyl-thiophenol,  $\text{HS}[2]\text{C}_6\text{H}_4[1]\text{COCH}_3$ , b.p. about 124–126° obtained from o-amino-acetophenone through the diazo-compound, gives *thio-indigo*, together with the corresponding dithio-compound (*Ger. Pat.* 198,509).

#### 4. Phenol Monocarboxylic Acids

Aromatic carboxylic acids which have a hydroxyl-group attached to the ring behave like phenols, as well as carboxylic acids, and are called phenolic carboxylic acids. On the other hand, those which have a hydroxyl group in the side-chain, behave like alcohols and carboxylic acids, and are aromatic alcoholic acids. They are very similar in their reactions to the aliphatic hydroxy-acids.

##### *Methods of formation of phenol-carboxylic acids*

A. From derivatives of carboxylic acids: (1) Amino-acids are converted into diazo-acids by the action of nitrous acid, and these are

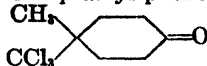
boiled in aqueous solution; (2) sulpho-benzoic and halogeno-benzoic acids are fused with alkalis; (3) ammonium salts of acids of the benzoic series are oxidised with hydrogen peroxide, giving rise to *o*-, *m*-, and *p*-hydroxybenzoic acids together (*Dakin*, J. Biol. Ch. 3, 419).

*B.* From compounds already containing a phenolic hydroxyl group: (4) When the homologues of phenol are fused with alkali, the methyl-groups attached to the ring are oxidised to carboxyl groups; (5) sulphates and phosphates of the homologues of phenol are oxidised, and the resulting phenol-carboxylic esters are hydrolysed; (6) phenol-aldehydes, which are rather resistant to oxidation, are fused with alkalis; (7) phenol-aldoximes are converted into hydroxy-nitriles and these are hydrolysed.

*C. Nuclear syntheses.*—(8) Carbon dioxide is passed through dry alkali phenates at a high temperature; *o*-derivatives are formed as a rule. This reaction will be dealt with in greater detail in connection with salicylic acid. (9) Phenols are boiled with carbon tetrachloride and alcoholic potash (*Hasse*, Ber. 10, 2185), preferably in the presence of copper, or copper compounds (Ger. Pat. 258,887):

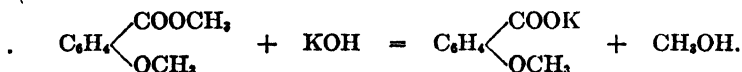


In most cases the carboxyl group enters the *p*-position relative to the hydroxyl group, but a certain amount of *o*-hydroxy-acid is also formed. This reaction is analogous to the synthesis of hydroxy-aldehydes from phenols, chloroform, and aqueous alkali, and there is a further analogy in the fact that carbon tetrachloride, in the presence of aluminium chloride, converts *p*-alkyl-phenols into keto-dihy-

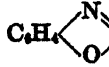
drobenzene derivatives (Vol. II, p. 118),  from which the phenols can be re-formed by reduction (*Zincke*, Ber. 41, 897).

(10) The amides, anilides, and thio-anilides of alkoxy-carboxylic acids are formed by the interaction of urea chloride, phenyl isocyanate, or phenyl mustard oil and phenol ethers (or thiophenol ethers) in carbon disulphide solution, in presence of aluminium chloride (*cf.* p. 289) (*Gattermann*, Ann. 244, 41; *Auwers*, Ber. 27, 1733).

*Reactions.* The phenol-monocarboxylic acids are monobasic, only the carboxylic hydrogen being replaced on neutralisation with alkaline carbonates. With caustic alkalis, phenate salts are formed, sometimes referred to as basic-salts, *e. g.*,  $\text{NaO} \cdot \text{C}_6\text{H}_4\text{CO}_2 \cdot \text{Na}$ . When these are acted upon by carbon dioxide, the neutral salts are re-formed. The dialkyl-derivatives behave similarly; only the alkyl-group attached to the carboxyl group is removed by the action of alkali, and an alkyl-ether-carboxylic salt is formed:



Hydroxy-carboxylic acids, particularly the di- and tri-hydroxy-acids, in the form of their carbomethoxy-compounds of chlorides, readily form polymolecular chains, of which the components are the anhydrides of the acids, by loss of water or hydrogen chloride. These compounds are called *depsides*, and resemble the tannins (Vol. II, p. 380). Some acylated phenol-carboxylic acids undergo partial rearrangement when partially hydrolysed, the acyl group migrating from the *p*- to the *m*-position (*Fischer*, Ber. 51, 45). When the azides (p. 360) of the hydroxy-acids are heated, isocyanates,  $\text{HO} \cdot \text{Ar} \cdot \text{N} : \text{CO}$ , are formed, which rearrange to heterocyclic compounds. Thus, salicylic azide gives *benzoxazolone*,

  $\text{C}_6\text{H}_4 \begin{array}{l} \text{N} \\ \text{O} \end{array} \text{C}(\text{OH})$ , and *o*-hydroxyphenyl-acetic and similar azides, give derivatives of *m*-benzoxazine (*Lindemann*, Ann. 451, 241; 464, 237).

*o*-Monohydroxy-carboxylic acids differ from the *m*- and *p*-compounds in being volatile in steam. Their aqueous solutions give a violet-blue colour with ferric chloride, and they dissolve in chloroform. The *m*-hydroxy-acids are distinguished by the Lindemann reaction with hot concentrated sulphuric acid; a reddish-brown colour is produced owing to the formation of hydroxy-anthraquinone (Lindemann, Ber. 18, 2142). They are more stable than the *o*- and *p*-acids. The latter break down into phenol and carbon dioxide simply on heating with concentrated hydrochloric acid. For the reactions of ethers and esters of these hydroxy-acids with hot water under pressure, see Schorigyn, Ber. 64, 274. All hydroxy-benzoic acids are decomposed into carbon dioxide and phenols on heating with lime.

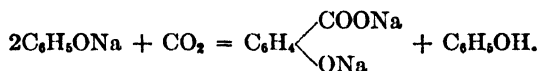
#### (A) Monohydroxy-monocarboxylic Acids

Salicylic acid, *o*-hydroxy-benzoic acid, is the most important member of this group. It is largely used in the dyestuff industry, and in medicine.

**MONOHYDROXY-BENZOIC ACIDS.** The three isomers required by theory are known.

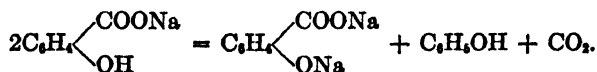
**Salicylic acid, *o*-hydroxy-benzoic acid,**  $\text{HO}[2]\text{C}_6\text{H}_4(1)\text{COOH}$ , m.p.  $155^\circ$ , occurs in the free state in the flowers of *Spiraea ulmaria*, and in the form of its methyl ester in oil of wintergreen, the essential oil of the *Ericacea*, *Gaultheria procumbens*, and in many other essential oils. It is obtained by the general methods for the formation of phenol-carboxylic acids: (1) from anthranilic acid; (2) from *o*-sulpho, *o*-chloro-, and *o*-bromobenzoic acids (Rosenmund, Ber. 53, 2226); (3) from *o*-cresol; (4) from saligenin, or salicylaldehyde; (5) from phenates by the action of carbon dioxide, or (6) carbon tetrachloride. It is also formed when coumarin, or indigo are fused with potash, and when copper benzoate is distilled.

**Industrial processes.**—Two methods are in use, both based on the combination of sodium phenate with carbon dioxide to form salicylic acid. (a) Dry sodium phenate is heated at  $180$ – $200^\circ$  in a current of carbon dioxide. Half the phenol distils over, and the other half is converted into disodium salicylate:



This is *Kolbe's process*. The mechanism of the process has been studied in detail by Austin and Johnson (Am. 54, 652; 55, 3031). Potassium phenate behaves differently from the sodium compound. At  $150^\circ$ , dipotassium salicylate and a certain amount of dipotassium-*p*-hydroxybenzoate is formed; with rising temperature the percentage of the *p*-salt increases, and at  $220^\circ$  it is the only product.

When the primary alkali salicylates are heated they behave as follows: monosodium salicylate at  $220^\circ$  gives disodium salicylate, phenol and carbon dioxide:



Monopotassium salicylate at  $220^\circ$  gives dipotassium-*p*-hydroxybenzoate, phenol, and carbon dioxide. At  $280^\circ$  monosodium *p*-hydroxybenzoate gives disodium salicylate, phenol, and carbon dioxide (Kupferberg, J. pr. 16, 425). *o*- and *p*-Hydroxy-benzoic acids can be separated by means of acetylene dichloride,  $\text{C}_2\text{H}_2\text{Cl}_2$  (Mann, Chem. Ztg. 56, 452).

(b) The second process, invented by Schmidt (Ger. Pats. 29,939 and 38,742),

involves the use of pressure. In an autoclave, carbon dioxide and sodium phenate form sodium phenol-carbonate,  $\text{PhO} \cdot \text{COONa}$ , which, at  $120^\circ$ , partly dissociates into carbon dioxide and sodium phenate. These combine to give sodio-phenol-*o*-carboxylic acid,  $\text{NaO}[2]\text{C}_6\text{H}_4[1]\text{CHO}$ . The two steps of this process are contracted into one if carbon dioxide acts on sodium phenate at  $120$ – $140^\circ$  under pressure. By this method, all the phenol used is converted into the acid. The imperfect conversion in *Kolbe's process* seems to be due to a secondary reaction which takes place at the high temperature used. Sodio-phenol-*o*-carboxylic acid and sodium phenate react to give disodium salicylate and free phenol (*Tijmstra*, *Ber.* 38, 1375; 39, 14; *Stuiter*, *Ber.* 45, 59; *Brunner*, *Ann.* 351, 313).

**History.** *Piria* discovered salicylic acid in 1838, by oxidising salicylaldehyde by fusing it with potash (*Ann.* 30, 165). In 1843 *Cahours* discovered that oil of wintergreen was chiefly made up of methyl salicylate (*Ann.* 53, 332). In 1853, *Gerland*, at the suggestion of *Hofmann*, showed that anthranilic acid is converted into salicylic acid by the action of nitrous acid (*Ann.* 86, 147). The acid was first synthesised from phenol, sodium, and carbon dioxide by *Kolbe* and *Laute-mann* in 1860 (*Ann.* 115, 201). In 1874, *Kolbe* noticed that it was readily formed when carbon dioxide was passed over dry sodium phenate, and this made possible its manufacture on a large scale.

**Properties and reactions.**—Salicylic acid crystallises from alcohol in colourless prisms, and from hot water in long needles. It has a sweet, but also acid taste. It dissolves in 400 parts of water at  $15^\circ$ , and in 12 parts at  $100^\circ$ , and is freely soluble in chloroform. When heated by itself it is converted into phenyl salicylate, or *salol*, and into *xanthone*. It is reduced by sodium and amyl alcohol, first to cyclohexanone-carboxylic acid, and then the ring opens and *n*-pimelic acid is formed (*Einhorn*, *Willstätter*, *Ber.* 27, 331) (p. 32). The aqueous solution of the acid gives a violet colour with ferric chloride (*Mann*, *Ch. Ztg.* 56, 452), "hydroferri-salicylo-chloric acid" being formed,  $\text{H}_2\{\text{Fe}(\text{C}_6\text{H}_4[\text{O}]\text{COO})\text{Cl}_2\}\text{Cl}_2$ , (*Claasz*, *Ar. Pharm.* 253, 342, 360). Salicylic acid is a powerful antiseptic and prevents putrefaction and fermentation, a fact first shown by *Kolbe* (*J. pr.* [2], 10, 9). It is used in medicine, both in the free state, and in the form of its salts, esters, and other compounds, as a specific for rheumatoid arthritis.

**Salicylates.**—Sodium salicylate,  $\text{HO} \cdot \text{C}_6\text{H}_4\text{COONa}$ , is a crystalline powder, with an unpleasant, sweetish taste. The basic calcium salt,  $(\text{OC}_6\text{H}_4\text{CO}_2)_2\text{Ca} + \text{H}_2\text{O}$ , is very difficultly soluble in water, and separates out when salicylic acid is boiled with lime water. It is used for separating salicylic acid from *m*- and *p*-hydroxy-benzoic acids.

**Esters, ethers, and ether-esters.** Methyl salicylate,  $\text{HO} \cdot \text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$ , m.p.  $-1^\circ$ , b.p.  $224^\circ$ ,  $d_4^{20}$  1.197, is the chief constituent of oil of wintergreen, the essential oil of *Gaultheria procumbens*, and occurs in several other plants (*Schimmel's Ber.* 29, R 511), sometimes free, and sometimes in the form of a glucoside. (*Bourgelot*, *C.r.* 122, 1002). Methyl *O*-methyl salicylate,  $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$ , b.p.  $245^\circ$ , is obtained by the action of methyl iodide and alcoholic potash on methyl salicylate, or by the action of dimethyl sulphate on sodium salicylate (*Sachs*, *Ber.* 40, 2718). When hydrogenated under high pressure it gives phenol if no solvent is present, and cyclohexanol, in almost quantitative yield, in methyl alcohol solution. *O*-Methyl-salicylic acid,  $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4\text{COOH}$ , m.p.  $100$ – $101^\circ$ , is formed when the methyl ester of this acid is boiled with potash, or by oxidising *o*-anethole with potassium permanganate (*Claesen*, *Ann.* 418, 69). It decomposes at  $200^\circ$  into anisole and carbon dioxide (p. 193). Its chloride,  $\text{CH}_3\text{O}[2]\text{C}_6\text{H}_4\text{COCl}$ , b.p.  $145^\circ$  (17 mm.), is obtained from the acid by the action of thionyl chloride (*Fischer*, *C.* 1902, II, 216). Nitrile, m.p.  $5^\circ$ , b.p.  $263^\circ$ . For the preparation of 5-sulpho-salicylic acid from salicylic acid and dimethyl sulphate, see *Simon*, *C.r.* 177, 533.

Phenyl salicylate, *salol*,  $\text{HO} \cdot \text{C}_6\text{H}_4\text{COOC}_6\text{H}_5$ , m.p.  $43^\circ$ , b.p.  $172^\circ$  (12 mm.)

can be prepared: by heating salicylic acid by itself at 200–220°, when water and carbon dioxide are liberated and salol formed; it can also be obtained by the action of phenol and phosphorus oxychloride on salicylic acid, from polysalicylide by heating with phenol, and by the action of carbonyl chloride on sodium salicylate and sodium phenate. It is used as an antiseptic. When heated it is converted into diphenylene-ketoxide, or *xanthone*. *p*-Acetamino-phenyl salicylate, *salophen*, m.p. 187°, has been prepared by *Brewster* (Am. 40, 1136) by reduction and acetylation of *p*-nitrophenyl salicylate. *Sodio-salol*,  $\text{NaO} \cdot \text{C}_6\text{H}_4\text{CO}_2 \cdot \text{C}_6\text{H}_5$ , when heated to 280–300°, gives the sodium salt of *O*-phenyl-salicylic acid, *phenoxybenzoic acid*,  $\text{C}_6\text{H}_5\text{O} \cdot \text{C}_6\text{H}_4\text{COOH}$ , m.p. 113°, a substance which is also obtained by heating *o*-chlorobenzoic acid with alkali phenates in the presence of copper (*Ullmann*, Ber. 38, 2111). The solution of this acid gives no colour with ferric chloride. Phenyl phenyl-salicylate  $\text{C}_6\text{H}_5\text{O}[2]\text{C}_6\text{H}_4[1]\text{COOC}_6\text{H}_5$ , m.p. 100°, is formed when phenyl carbonate,  $(\text{C}_6\text{H}_5\text{O})_2\text{CO}$ , is heated with sodium carbonate, phenol and carbon dioxide being driven off (*Fosse*, C.r. 136, 1074).

**Acetyl-salicylic acid**,  $\text{CH}_3\text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4\text{COOH}$ , m.p. 135°, but the m.p. is not sharp. It is widely used as an analgesic under the name of *aspirin* and other proprietary names. The melting point seems to depend on the solvent from which it is crystallised, and on traces of moisture, which bring about slight hydrolysis (*Capelli*, Giorn. Chimia appl. 2, 379). It forms an addition product with urea, m.p. 88–90°, called *diafor* (Ger. Pat. 274,046). Its anhydride, m.p. 85°, is obtained by the action of thionyl chloride or carbonyl chloride on the acid dissolved in pyridine (Ger. Pat. 201,325). In absence of pyridine, acetyl-salicylic chloride, m.p. 43°, is formed. This combines with methyl salicylate in pyridine to form methyl acetyl-salicylo-salicylate, forming crystals, m.p. 82–84°, which have an aromatic odour (*Lewicka*, C. 1928, I, 190). Esters of acetyl-salicylic acid have been prepared by adding alcohols slowly to a cooled mixture of the acid and quinine (*Wolffenstein*, Ber. 46, 582). Methyl ester, m.p. 48° (*Archetti*, Boll. Pharm. 55, 718). See also *Sah*, Tsing Hua Rep. 2, 13. When acetyl-salicylic acid is heated to 355° in a vacuum, it decomposes into acetic acid and *xanthone* (*Spektor*, C. 1934, II, 1685). For the introduction of other acyl groups into the OH-group of salicylic acid, see *Einhorn*, Ber. 44, 3309.

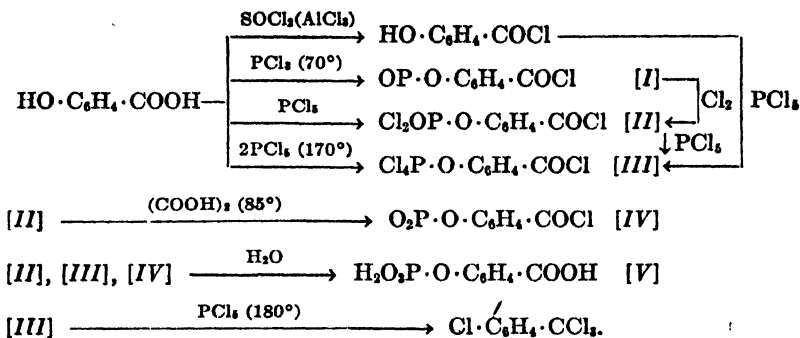
**Carbomethoxy-salicylic acid**,  $\text{CH}_3\text{OCO} \cdot \text{O}[2]\text{C}_6\text{H}_4[1]\text{COOH}$ , m.p. 135° (decomp.), has been prepared by *Fischer* (Ber. 42, 218) from salicylic acid, chloro-carbonic ester, and dimethylaniline. **Salicylo-acetic acid**,  $\text{C}_6\text{H}_4(\text{OCH}_2\text{COOH})\text{COOH}$ , m.p. 190° is an oxidation product of aldehydo-phenoxy-acetic acid (p. 345), and can also be obtained by the action of ethyl chloroacetate on the sodium salts of various acyl derivatives of salicylic acid, followed by hydrolysis. The esters of this acid condense to ketocumaran-carboxylic esters under the influence of sodium (*Bischoff*, Ber. 33, 1398; Ger. Pat. 110,376).

**Salicylic chloride, salicyloyl chloride, *o*-hydroxy-benzoyl chloride**, m.p. 18°, b.p. 59° (1 mm.), is a compound which has been very difficult to prepare. *Kopetschni* and *Karczag* succeeded in obtaining it in the pure state by the action of thionyl chloride on sodium salicylate (Ber. 47, 235). The best method is to treat salicylic acid with thionyl chloride in the presence of traces of aluminium chloride (*Kirpal*, Ber. 63, 3190). It forms colorless needles, which possess a not unpleasant odour, and break down on heating. It has therefore been suggested that the compound might be prepared in boiling benzene (Ger. Pats. 123,502 and 284,161). Phosphorus chlorides, rather surprisingly, give phosphorus derivatives of salicylic acid (see below); chloro-derivatives of salicyloyl chlorides can only be formed from the derivatives of salicylic acid in which the phenol group is protected by an ortho-effect from the action of phosphorus pentachloride (*Anschütz*, Ann. 228, 308; 346, 299, 300; 454, 82, 95).

***o*-Cresotic chloride**,  $\text{HO}[2]\text{C}_6\text{H}_3[3]\text{CH}_2[1]\text{COCl}$ , m.p. 28°; 3-chloro- and 3-nitro-salicyloyl chlorides, m.p. 63°, and 61°; 3,5-dichloro-, 3,5-dibromo-, and 3,5-diiodo-salicyloyl chlorides, m.p. 79°, 86°, and 98°; 3,5-dinitro-salicyloyl chloride, m.p. 70°.

**DERIVATIVES OF SALICYLIC ACID CONTAINING PHOSPHORUS.** For nomenclature, see (8)\* where a general survey is given. The formation and reactions of these substances are shown in the following scheme:

\* Numbers in parentheses refer to references quoted at the end of this section, p. 358.



***m*-Phosphorisal chloride**, 2-chloroformyl-phenyl metaphosphite, "salicylo-phosphorous acid chloride," formula *I* above, m.p.  $37^\circ$ , b.p.  $127^\circ$  (11 mm.), is obtained by the action of phosphorus trichloride on salicylic acid (ref. 1 below); all the substituted salicylic acids behave similarly (7, 9). For proof of constitution, see (10).

**Phosphosal chloride**, 2-chloroformyl-phenyl dichloro-phosphate, 2-chloro-formyl-phenyl-phosphoric dichloride, b.p.  $168^\circ$  (11 mm.), formula *II* above, is obtained by the action of phosphorus pentachloride on salicylic acid (11), or by the action of chlorine or phosphorus pentachloride on *m*-phosphorisal chloride (2, 6); for proof of its constitution, see (12), and for the action of heat on it, see (5). It gives *o*-phosphorisal chloride, (see below) with phosphorus pentachloride at  $170^\circ$  (3). For its other reactions, see the above scheme.

***o*-Phosphosal chloride**, 2-chloroformyl-phenyl-tetrachloro-phosphate, 2-chloro-formyl-phenyl-phosphoric tetrachloride, formula *III* above, b.p.  $179^\circ$  (11 mm.),  $133^\circ$  (0.003 mm.), is obtained from phosphosal chloride and phosphorus pentachloride (see above), and by the action of phosphorus pentachloride on salicyloyl chloride (13); the latter reaction establishes its constitution. When heated with phosphorus pentachloride in a sealed tube at  $180^\circ$ , it gives *o*-chloro-benzotrichloride  $\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{CCl}_3$ , m.p.  $30^\circ$ , b.p.  $130^\circ$  (11 mm.).

**Meta-phosphosal chloride**, 2-chloroformyl-phenyl metaphosphate, formula *IV* above, m.p.  $95^\circ$ , b.p.  $171^\circ$  (11 mm.), is prepared from phosphosal chloride and anhydrous oxalic acid at  $85^\circ$  (8, 16). A very similar compound has the composition  $\text{C}_6\text{H}_4\text{O}_6\text{ClP}$ , m.p.  $82^\circ$  (14, 17).

**Phosphosal**, *O*-phospho-salicylic acid, formula *V* above, m.p. between  $140$  and  $154^\circ$ , is formed as shown in the scheme above. It can be distinguished from salicylic acid by the fact that its aqueous solution only reacts with ferric chloride on boiling. For its salts and molecular compounds, see (15, 18, 20).

**Literature.**—(1) *R. Anschütz*, Ann. 239, 301; (2) *ibid.*, 304; (3) *ibid.*, 319; (4) *ibid.*, 321; (5) *ibid.*, 330; (6) Ann. 346, 286; (8) *ibid.*, 293; (9) Ber. 30, 221; (10) *L. Anschütz*, Ann. 439, 265; (11) *ibid.*, 269; (12) Ann. 454, 72; (13) *ibid.*, 73; (14) *ibid.*, 76; (15) *ibid.*, 78; (16) *ibid.*, 100; (17) *ibid.*, 101; (18) *ibid.*, 103; (19) *ibid.*, 104, note; (20) *Chasanowitsch*, Ber. 20, 1165.

**OTHER O-DERIVATIVES OF SALICYLOYL CHLORIDE.** If the hydrogen atom of the phenolic hydroxy-group is protected by substitution, phosphorus pentachloride gives *O*-substituted salicyloyl chlorides; e.g., ***O*-methyl-salicyloyl chloride**, *o*-methoxy-benzoyl chloride, see p. 356. **Aceto-salicyloyl chloride**, *o*-acetoxy-benzoyl-chloride, *aspirin chloride*,  $\text{CH}_3\text{CO} \cdot \text{O} \cdot [2]\text{C}_6\text{H}_4[1]\text{COCl}$ , m.p.  $43^\circ$ , b.p.  $135^\circ$  (12 mm.). **Carbomethoxy-salicyloyl chloride**,  $\text{CH}_3\text{OCO} \cdot \text{O} \cdot [2]\text{C}_6\text{H}_4[1]\text{COCl}$ , b.p.  $107\text{--}110^\circ$  (0.1 mm.).

**ANHYDRO-DERIVATIVES OF SALICYLIC ACID.** **Salicyloyl-salicylic acid**, *diplosal*,  $\text{HO}[2]\text{C}_6\text{H}_4[1]\text{COO}[2]\text{C}_6\text{H}_4[1]\text{COOH}$ , m.p.  $148^\circ$ , is the simplest aromatic depside. It is obtained by the carefully regulated action of thionyl chloride, phosphorus trichloride, carbonyl chloride, etc., on salicylic acid or salicylates. It is used in medicine (Ger. Pat. 214,044). **Acetyl-salicyloyl-salicylic acid**,  $\text{CH}_3\text{CO} \cdot \text{OC}_6\text{H}_4\text{CO} \cdot \text{OC}_6\text{H}_4\text{COOH}$ , m.p.  $161\text{--}162^\circ$ , is obtained from ethyl acetyl-salicylo-carbonate, or from the mixed anhydride of acetyl-salicylic and salicylic acids, by

the action of tertiary bases (*Einhorn*, Ber. 44, 437). Salicyloyl-salicylic acid gives a chloride, m.p. 99°, with thionyl chloride. Anilide, m.p. 160.5°. When the chloride is boiled with dimethylaniline it gives  $\alpha$ -disalicylide (see below) (*Anschütz*, J. pr. 105, 150).

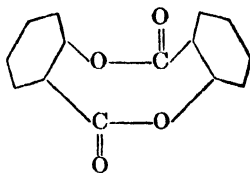
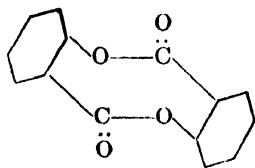
Disalicylic acid,  $O(C_6H_4COOH)_2$ , m.p. 230° (decomp.) is obtained from *o*-tolyl-salicylic acid,  $COOH.C_6H_4.O[2]C_6H_4.[1]CH_3$ , by oxidation with potassium permanganate. Chloride, m.p. 161°. Analogous acids are produced by oxidation of *m*- and *p*-tolyl-salicylic acids. When heated with concentrated sulphuric

acid, or acetyl chloride, xanthone-*o*-carboxylic acid,  $C_6H_4 \begin{array}{c} \diagup CO \diagdown \\ \diagdown O \diagup \end{array} C_6H_4[4]COOH$ , is formed with ring closure. The same compound is produced by treating the acid chloride with anhydrous oxalic acid (*Anschütz*, Ber. 55, 680).

**SALICYLIDES.** The simplest intramolecular anhydride of salicylic acid,  $C_6H_4 \begin{array}{c} \diagup CO \diagdown \\ \diagdown O \diagup \end{array}$ , is unknown, but a number of polymers of this simple salicylide have been prepared (*Anschütz*, J. pr. 105, 158; Ann. 439, 1).

**DISALICYLIDES.** Acetyl-salicylic acid, and its anhydride, when heated in a vacuum, give acetic acid, acetic anhydride, salicylic acid, and a mixture of two disalicylides, which can be separated by means of chloroform. One is  $\alpha$ -disalicylide, m.p. 213°, the other  $\beta$ -disalicylide, m.p. 199–200°. They are also obtained by heating tetra- or poly-salicylides in a vacuum, or by passing carbonyl chloride through a pyridine solution of salicylic acid (*Anschütz*, Ber. 52, 1875; 54, 2951; Ann. 439, 1). The  $\alpha$ -form can be obtained by boiling the chloride of salicyloyl-salicylic acid with diethylaniline.  $\alpha$ -Disalicylide gives methyl salicyloyl-salicylate when heated to 100° with methyl alcohol. This compound is readily soluble. The  $\beta$ -disalicylide remains unchanged when treated in this way.  $\alpha$ -Disalicylide gives salicyloyl-salicyl-amide,  $HOC_6H_4CO \cdot OC_6H_4CONH_2$ , m.p. 185–189°, with ammonia. On heating this amide isomerises to *disalicyloyl-imide*, m.p. 185–189°,  $(HOC_6H_4CO)_2NH$  (*Anschütz*, Ann. 439, 5).  $\beta$ -Disalicylide is only attacked by ammonia with difficulty.

The formulation of the disalicylides is still uncertain. *Anschütz* (J. pr. 105, 161) regarded the  $\alpha$ -form as a cyclic salicylic double ester, analogous with lactide, and assumed a different constitution for the  $\beta$ -form. Both disalicylides, however, may have a lactide structure, and differ stereochemically, one being a "sessile," and the other a "tub"-like form, as in the case of cyclohexane derivatives (private communication from *F. Höhn*).



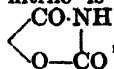
Tetrasalicylide,  $O \cdot C_6H_4CO \cdot O \cdot C_6H_4 \cdot CO$   
 $\begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} C_6H_4O \cdot CO \cdot C_6H_4 \cdot O$ , m.p. 260°, and polysalicylide,

$(C_7H_5O_2)_n$ , m.p. 322–325°, are formed by the action of phosphorus oxychloride on salicylic acid in xylene, and from salicyloyl chloride by heating under ordinary pressure (*Anschütz*, J. pr. 105, 158). The two compounds are separated by means of boiling chloroform, with which tetrasalicylide forms a compound, *salicylide-chloroform*,  $(C_7H_5O_2)_4 \cdot 2CHCl_3$ , crystallising in beautiful quadratic octahedra, and containing 35% of loosely combined chloroform of crystallisation. It is used industrially for the preparation of pure *chloroform* (*Anschütz*, Ann. 273, 94; Vol. I, p. 290). Cresotic acids (Ber. 35, 3644) and *o*-halogeno-salicylic acids react similarly. For the molecular weight of tetrasalicylide, see *Schroeter*, Ann. 367, 164.

**Salicylamide**,  $HO \cdot C_6H_4CONH_2$ , m.p. 138° (*Claisen*, Ber. 24, 138). When

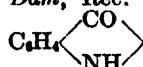


salicylamide in pyridine solution is acted upon by carbonyl chloride, salicylic nitrile is obtained (see below), together with carbonyl-salicylamide,  $C_6H_4$ -



, m.p. 227°, which is better prepared by the action of ethyl chlorocar-

bonate on salicylamide in pyridine solution (*Einhorn*, Ber. 35, 3647). The O-acyl-salicylamides are unstable, and readily changed into N-acyl compounds when heated with pyridine, or fused:  $\text{AcOC}_6\text{H}_4\text{CONH}_2 \longrightarrow \text{HOC}_6\text{H}_4\text{CONHAc}$ . This rearrangement is reversible under certain conditions. Thus the N-acyl compound reverts to the O-compound when boiled with acetic acid (*Auwers*, Ber. 40, 3506; *Anschütz*, Ann. 442, 20). When acted upon by bromine and alkali, salicylamide undergoes a rearrangement to carbonyl-aminophenol (p. 205), and this is further brominated to dibromo-carbonyl-aminophenol (*van Dam*, Rec. 18, 408). Salicyl-anilide,  $C_6H_4(\text{OH})\text{CONHC}_6\text{H}_5$ , gives acridone,



, when heated alone, probably through a rearrangement into

phenyl-anthranilic acid (p. 325) (*Pictet*, Ber. 29, 1189). For condensation products of salicyloyl chloride and anthranilic acid, see Ger. Pat. 284,735. Salicylic nitrile,  $\text{HO}\cdot\text{C}_6\text{H}_4\text{CN}$ , m.p. 98°, is obtained from salicylaldehyde and acetic anhydride (*Bone*, J. 63, 1; *Beckmann*, Ber. 26, 2621). It is esterified only with difficulty by methyl alcohol and ethyl alcohol and hydrochloric acid, at temperatures below 100°. Salicylic hydrazide,  $\text{HO}\cdot\text{C}_6\text{H}_4\text{CONH}\cdot\text{NH}_2$ , m.p. 147° gives salicylic azide,  $\text{HO}\cdot\text{C}_6\text{H}_4\text{CON}_3$ , m.p. 27°, with nitrous acid. The latter is a crystalline compound with a pungent odour. Salicyluric acid,  $\text{HO}\cdot\text{C}_6\text{H}_4\text{CO}\cdot\text{NHCH}_2\text{COOH}$ , m.p. 170°, is found in the urine when salicylic acid has been administered, and has been synthesised from salicylic azide or carbomethoxy-salicyloylchloride, and glycocoll (*Fischer*, Ber. 42, 219; *Bertagnini*, Ann. 97, 250). Ethyl ester, b.p. 88° (*Schroeter*, Ber. 52, 2224).

**SULPHUR DERIVATIVES OF SALICYLIC ACID.** The following are derivatives substituted in the *carboxyl group*:

**Thiol-salicylic acid**,  $\text{HOC}_6\text{H}_4\text{COSH}$ , white crystals, m.p. 33°, with an odour reminiscent of phosphorus, is obtained by the action of an alcoholic solution of sodium hydrogen sulphide,  $\text{NaHS}$ , on acetyl-salicyloyl chloride (Ger. Pat. 365,212); **carbi-thiosalicylic acid**,  $\text{HOC}_6\text{H}_4\text{CSSH}$ , bright orange needles, m.p. 48–50°, is formed when hydrogen chloride is passed into salicylaldehyde and hydrogen sulphide in benzene solution. Methyl ester, yellow needles, m.p. 10–20°; dimethyl-ether ester, m.p. 43–44° (*Hoehn*, J. pr. 82, 488).

Derivatives of salicylic acid with sulphur substituted in the *hydroxyl group* include *thiosalicylic acid* and its derivatives, which are of considerable industrial importance as they are readily converted into indigoid sulfur dyes; see thioindigo, Vol. IV, and *Friedländer*, Ann. 351, 390.

**Thiosalicylic acid**,  $\text{HS}[2]C_6H_4[1]COOH$ , m.p. 164° (indefinite), is obtained (1) by treating diazotised anthranilic acid with potassium xanthate (p. 124), potassium thiocyanate, or alkali sulphides (Ger. Pat. 205,450; *Allen*, Org. Synth. 12, 76), the resulting compounds,  $\text{CO}_2\text{HC}_6\text{H}_4\text{S}\cdot\text{C}\cdot\text{SOC}_6\text{H}_5$ ,  $\text{CO}_2\text{HC}_6\text{H}_4\text{SCN}$ ,  $(\text{CO}_2\text{HC}_6\text{H}_4)_2\text{S}_2$  (see below), being subsequently reduced. (2) By heating *o*-chlorobenzoic acid with alkali hydrogen sulphides, or alkali sulphides in the presence of copper powder (Ger. Pat. 189,200). (3) By reduction of the unstable *o*-sulpho-benzoic dichloride (p. 332). (4) By heating metallic derivatives of thiophenol (p. 214) with carbon dioxide under pressure; the resulting phenyl-thiocarbonate undergoes a rearrangement in the same way as in the preparation of salicylic acid, when the temperature is raised to 240–270° (Ger. Pat. 514,507).

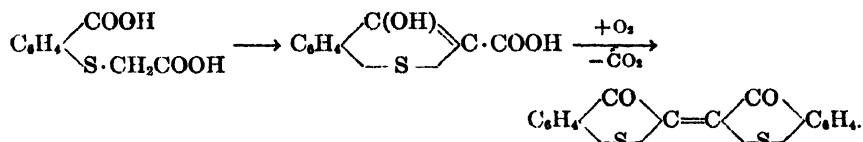
Thiosalicylic acid is readily oxidised to dithiosalicylic acid,  $\text{S}_2(C_6H_4\text{COOH})_2$ , (*List*, Ber. 31, 1665). It condenses with benzene in the presence of sulphuric acid

to form *thioxanthone* (*Prescott*, J. 99, 640). **Di-thiosalicylide**,  $C_6H_4 \begin{array}{c} \diagup \text{CO}\cdot\text{S} \\ \diagdown \text{S}\cdot\text{CO} \end{array} C_6H_4$ ,

m.p. 175°, is formed by heating acetyl-thiosalicylic acid at low pressures. Phenyl disulphide, and a substance with the formula  $C_{14}H_{10}S_2$  are formed at the same time (*Anschütz*, Ber. 47, 2733; 52, 1876). Phenyl thiosalicylate,  $HSC_6H_4CO_2C_6H_5$ , m.p. 91°, is obtained from thiosalicylic acid, phenol, and phosphorus oxychloride,  $POCl_3$  (*Mayer*, Ber. 42, 1134).

Methyl-thiosalicylic acid,  $CH_3SC_6H_4COOH$ , m.p. 169°, is obtained by the action of dimethyl sulphate or methyl iodide on alkaline solutions of thiosalicylic acid, dithiosalicylic acid, *o*-thiocyano-benzoic acid, etc. When fused with alkalis, preferably in the presence of a condensing agent such as sodium cyanamide, sodio-lead, etc., it gives *thio-indoxyl* (Ger. Pat. 200,200). Phenyl-thiosalicylic acid,  $C_6H_5SC_6H_4COOH$ , m.p. 167°, obtained from *o*-chlorobenzoic acid and sodium thiophenate in the presence of copper powder, gives *thio-xanthone* when heated with concentrated sulphuric acid or acetic anhydride (*Graebe*, Ann. 263, 2; *Goldberg*, Ber. 37, 4526; *Weedon*, Am. J. 33, 386). Acetylene-bis-thiosalicylic acid,  $CO_2HC_6H_4S \cdot CH:CH \cdot SC_6H_4COOH$ , is obtained by the action of acetylene dichloride on alkali thiosalicylates, and gives *thio-indigo* with acidic condensing agents (Ger. Pats. 205,324 and 237,773).

*o*-Carboxyphenyl-thioglycolic acid,  $HOCO[1]C_6H_4[2]S \cdot CH_2COOH$ , m.p. 213°, is obtained (1) from thiosalicylic acid and monochloroacetic acid, (2) from thioglycolic acid and *o*-diazo-benzoic acid (p. 124). Its nitrile, m.p. 140°, is obtained by the action of monochloroacetic acid on amino-thiophenol, with subsequent replacement of the amino-group, first by the diazo-group, and finally by CN (*Friedländer*, Ann. 351, 412). Hot alkali converts carboxyphenyl-thioglycolic acid or its nitrile into *thio-indoxyl-carboxylic acid* which readily gives *thio-indigo* by loss of carbon dioxide and oxidation:



Diphenylsulphide-*o,o*-dicarboxylic acid,  $S(C_6H_4CO_2H)_2$ , m.p. 230°, is obtained by heating thiosalicylic acid with *o*-chlorobenzoic acid and copper powder (*Mayer*, Ber. 43, 588). Chloro-selenophenol-*o*-carboxylic acid,  $ClSe[2]C_6H_4COOH$ , is obtained by the action of thionyl chloride on diseleno-salicylic acid,  $Se_2(C_6H_4COOH)_2$ . Its chloride, m.p. 65–66°, gives the chloride (m.p. 122–123°) of *o*-seleno-cyano-benzoic acid, m.p. 185° (decomp.), with silver cyanide. Diphenyl-diselenide-di-*o*-carboxylic acid, di-seleno-salicylic acid,  $(SeC_6H_4COOH)_2$ , m.p. 234–235°, is obtained by the action of potassium selenide on diazotised anthranilic acid in an atmosphere of carbon dioxide (*Lesser*, Ber. 46, 2640; 47, 2507).

**SUBSTITUTED SALICYLIC ACIDS.** Of the mono-substituted salicylic acids, the 5-derivatives are the most readily formed, followed by the 3-derivatives. Hence, in the case of disubstituted acids, the 3,5-compounds, in which the substituents occupy the *o*- and *p*-positions to OH, are the most readily formed.

5-Chloro-salicylic acid, m.p. 172°.

5-Bromo-salicylic acid, m.p. 164°.

5-Iodo-salicylic acid, m.p. 196°.

5-Nitro-salicylic acid, m.p. 228°.

4-Nitro-salicylic acid, m.p. 235° has been prepared from 4-nitro-2-acetaminotoluene by the following steps: oxidation of the methyl group, hydrolysis, replacement of  $NH_2$  by OH (*Kondo*, Pharm. Japan, 1922). 5-Nitroso-salicylic acid, m.p. 162–163° (decomp.), bluish-green crystals, is formed by boiling 5-nitroso-methyl-anthranilic acid (p. 325) with sodium hydroxide or sulphuric acid, or by treating sodium salicylate with a solution of copper sulphate and sodium nitrite (*Gulinov*, Zhurnal, 5, 225). Its methyl ester forms bright blue crystals, m.p. 89–90°. The acid may be regarded as a quinone-oxime-carboxylic acid (p. 202) (*Houben*, Ber. 42, 2757; 53, 2352). 5-Thiocyano-salicylic acid, m.p. 167–168°, has been prepared from 5-amino-salicylic acid by diazotising and substituting CNS for the diazo-group. It gives 5-mercapto-salicylic acid, m.p. 148°, on reduction (*Kaufmann*, Ber. 58, 1556).

- 3-Chloro-salicylic acid, m.p. 178°.  
 3-Bromo-salicylic acid, m.p. 220°.  
 3-Iodo-salicylic acid, m.p. 193°.  
 3-Nitro-salicylic acid, m.p. 144° (*Hirsch*, Ber. 33, 3238).

3-Nitro-salicylic acid has been synthesised from nitro-malonaldehyde and acetoacetic ester (p. 25).

- 3,5-Dichloro-salicylic acid, m.p. 214°.  
 3,5-Dibromo-salicylic acid, m.p. 223°.  
 3,5-Diiodo-salicylic acid, m.p. 220-230° (decomp.).  
 3,5-Dinitro-salicylic acid, m.p. 173°.

3,5-Dichloro-salicylic anhydride, m.p. 187°, has been obtained by the interaction of the corresponding chloride and the silver salt (*Anschütz*, Ber. 30, 223; Ann. 346, 307). Other halogeno-salicylic acids have been prepared by *Lassar-Cohn* (Ber. 38, 3294). For the chlorides of substituted salicylic acids, see p. 357.

3-Amino-salicylic acid,  $\text{NH}_2[\text{C}_6\text{H}_4][2](\text{OH})\text{COOH}$  (*Zahn*, J. pr. 61, 532). 5-Amino-salicylic acid,  $\text{NH}_2[\text{C}_6\text{H}_4][2](\text{OH})\text{COOH}$ , is best prepared by the reduction of benzene-azo-salicylic acid,  $\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ , (*Puxeddu*, Gazz. 36, II, 87). Its diazo-compound gives *diamond black* when combined first with  $\alpha$ -naphthylamine, and then with  $\alpha$ -naphthol sulphonic acid and 5-hydrazino-salicylic acid,  $\text{NH}_2\text{NHC}_6\text{H}_4(\text{OH})\text{COOH}$ , m.p. 148°, on reduction (*Fischer*, Ber. 32, 81; C. 1900, I, 205). 5-Diethyl-glycocol-amino-salicylic methyl ester,  $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4(\text{OH})\text{COOCH}_3$ . Its hydrochloride, *nirvanin*, is a local anaesthetic (*Einhorn*, Ann. 311, 154).

Sulpho-salicylic acid,  $(\text{SO}_3\text{H})\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ , and nitro-sulpho-salicylic acid, see *Hirsch*, Ber. 33, 3238; *Cohn*, J. pr. 61, 545; *Meldrum*, Indian J. 7, 887, 893. Amino-sulpho-salicylic acid is obtained by the action of sodium bisulphite on nitro-salicylic acid (Ger. Pat. 123,115).

1,3- and 1,4-HYDROXY-BENZOIC ACIDS. *m*- and *p*-Hydroxybenzoic acids are obtained from the corresponding amino- and halogeno-benzoic acids by methods 1 and 2 (p. 353). *p*-Hydroxybenzoic acid is formed along with salicylic acid from phenol by methods 8 and 9 (p. 354). Many resins yield *p*-hydroxy-benzoic acid when fused with potash.

*m*-Hydroxy-benzoic acid,  $\text{HO}[\text{C}_6\text{H}_4][1]\text{COOH}$ , m.p. 200°, sublimes. *m*-Methoxy-benzoic acid,  $\text{CH}_3\text{O}[\text{C}_6\text{H}_4]\text{COOH}$ , m.p. 110°, is formed in the oxidation of *m*-cresol methyl ether with permanganate. *m'*-Hydroxy-*m*-benzoyloxy-benzoic acid, *m*-diplosal,  $\text{HO}[\text{C}_6\text{H}_4][1]\text{CO}\cdot\text{O}[\text{C}_6\text{H}_4][1]\text{COOH}$  (p. 358), m.p. 199° (*Anschütz*, Ann. 442, 45). *o*-Methylamino-*m*-methoxybenzoic methyl ester, *damascenin*, m.p. 26°, occurs in the oil of *Nigritella suaveolens*, and is prepared synthetically from *m*-methoxy-benzoic acid by introducing  $\text{NO}_2 \rightarrow \text{NH}_2 \rightarrow \text{NHCH}_3$  in the 2-position (*Ewins*, J. 101, 544), or by degradation of 8-methoxy-quinoline (*Kaufmann*, Ber. 49, 578).

*p*-Hydroxy-benzoic acid,  $\text{HO}[\text{C}_6\text{H}_4][1]\text{COOH}$ , melts when anhydrous at 210°, decomposing partially into phenol and carbon dioxide. *Methyl ester*, m.p. 131°, b.p. 270-280° (*Hoessle*, J. pr. 49, 501). Two modifications of the *ethyl ester* are known; one, m.p. 110°, is formed when either is sublimed and cooled; the other, m.p. 126°, is formed when either is sublimed, but not cooled. On recrystallisation the former changes into the latter (*Kofler*, Mikrochemie, 9, 45). *p'*-Hydroxy-*p*-benzoyloxy-benzoic acid, *p*-diplosal, m.p. 277° (decomp.) (*Fischer*, Ann. 372, 47). Several *p*-hydroxy-benzoyl residues can join in ester fashion, and the substances thus obtained show a tendency, increasing with the length of the molecule, to form liquid-crystalline salts. Thus, the compound containing four benzene rings and acylated at one end, and esterified with the ethyl group at the other, melts at 187°, and remains a crystalline liquid up to a red heat, when it decomposes. *p*-Carbomethoxy-phenoxy-acetic methyl ester,  $\text{COOCH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{COOCH}_3$ , m.p. 92-93° (*Christiansen*, Am. 48, 460). *m*-Hydroxy-*p*-amino- and *m*-amino-*p*-hydroxy-benzoic methyl esters, m.p. 121°, and 142°, respectively (*Einhorn*, Ann. 311, 26) are put on the market under the names *orthoform* and *neo-orthoform*, respectively, as local anaesthetics. *p*-Mercapto-benzoic acid,  $\text{HS}[\text{C}_6\text{H}_4][1]\text{COOH}$ , m.p. about 250° (decomp.), is a readily oxidised powder, prepared by reducing *p*-chlorosulphonyl-benzoic acid in acetic-hydrochloric acid with zinc dust (*Smiles*, J. 121, 2022).

For the action of chlorine on the three hydroxy-benzoic acids, see *Zincke*, Ann. 261, 236. With phosphorus pentachloride, *m*- and *p*-hydroxy-benzoic acids behave in the same way as salicylic acid (p. 357).

**Anisic acid**, *p*-methoxy-benzoic acid,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_4[1]\text{COOH}$ , m.p.  $185^\circ$ , b.p.  $280^\circ$ , is, together with benzoic and salicylic acids, among the longest known of the organic acids. It is isomeric with methyl salicylate, with monomethyl compounds of hydroxy-benzoic acids in general, and with hydroxyphenyl-acetic acids. It is readily accessible, and many of its reaction products are known. It is obtained from *anethole* (*q.v.*), the principal constituent of anise oil, and some other essential oils, by oxidation with dilute nitric or chromic acids. A synthesis from *p*-bromo-anisole, magnesium, and carbon dioxide, has been carried out by *Bodroux* (C.r. 136, 377).

Its nitrile, m.p.  $62^\circ$ , b.p.  $257^\circ$ , has been prepared from *p*-nitro-benzonitrile and sodium methoxide, by the action of phosphorus pentachloride on anisamide, and by the action of cyanogen bromide and aluminium chloride on anisole (*Scholl*, Ber. 33, 1056; 36, 648; *Henry*, Belg., 1899, 582).

**History**.—Anisic acid was discovered by *Cahours* in 1839 (Ann. 41, 66), as an oxidation product of anise oil. *Kolbe* was the first to regard it as a methoxy-benzoic acid, because it decomposes into carbon dioxide and anisole when distilled with baryta (p. 193). *Saytzev* (1863) found that it gave an acid isomeric with, but different from, salicylic acid, when heated with hydriodic acid (Ann. 127, 129); this acid was later identified as *p*-hydroxy-benzoic acid. In 1867, *Ladenburg* prepared anisic acid by the hydrolysis of *p*-hydroxy-benzoic dimethyl ether-ester (Ann. 141, 241).

**HYDROXY-TOLUIC ACIDS**. **Cresotic acids**,  $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})\text{COOH}$ . Ten isomers are possible, and all are known (*Jacobsen*, Ber. 16, 1966). They are isomeric with the three hydroxy-phenyl-acetic acids (p. 364), the three methoxy-benzoic acids, the hydroxy-methyl-benzoic acids, and with phenyl-glycollic or mandelic acid. They are obtained: 1. from toluic acids, by methods (1) and (2); 2. from hydroxy-aldehydes by method (6); and 3. from cresols by methods (8) and (9) (p. 354). The first three acids in the following table are usually called *o*-, *m*-, and *p*-homosalicylic, or *o*-, *m*-, and *p*-cresotic acids.

#### Homosalicylic acids

$\text{CH}_3[3]\text{C}_6\text{H}_3[2,1](\text{OH})\text{COOH}$ , m.p.  $163^\circ$   
 $\text{CH}_3[4]\text{C}_6\text{H}_3[2,1](\text{OH})\text{COOH}$ , m.p.  $177^\circ$   
 $\text{CH}_3[5]\text{C}_6\text{H}_3[2,1](\text{OH})\text{COOH}$ , m.p.  $153^\circ$   
 $\text{CH}_3[6]\text{C}_6\text{H}_3[2,1](\text{OH})\text{COOH}$ , m.p.  $168^\circ$

#### Methyl-*m*-hydroxybenzoic acids

$\text{CH}_3[2]\text{C}_6\text{H}_3[3,1](\text{OH})\text{COOH}$ , m.p.  $145^\circ$   
 $\text{CH}_3[4]\text{C}_6\text{H}_3[3,1](\text{OH})\text{COOH}$ , m.p.  $206^\circ$   
 $\text{CH}_3[5]\text{C}_6\text{H}_3[3,1](\text{OH})\text{COOH}$ , m.p.  $210^\circ$   
 $\text{CH}_3[6]\text{C}_6\text{H}_3[3,1](\text{OH})\text{COOH}$ , m.p.  $184^\circ$

#### Methyl-*p*-hydroxybenzoic acids

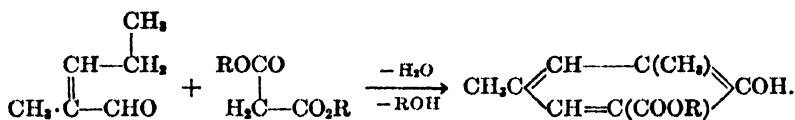
$\text{CH}_3[2]\text{C}_6\text{H}_3[4,1](\text{OH})\text{COOH}$ , m.p.  $177^\circ$      $\text{CH}_3[3]\text{C}_6\text{H}_3[4,1](\text{OH})\text{COOH}$ , m.p.  $174^\circ$

The homosalicylic acids with OH and COOH in *o*-positions resemble salicylic acid in giving a violet colour with ferric chloride, being freely soluble in chloroform, and being volatile in steam. For their reactions with phosphorus pentachloride, trichloride and oxychloride, see p. 357. Many homosalicylides or cresotides have been described, *e.g.*, *o*-, *m*-, and *p*-dicresotides, *o*- and *p*-tetracresotides, *m*-polycresotide. *o*-, but not *m*-Tetracresotide forms a compound with chloroform similar to salicylide-chloroform, known as *o*-homosalicylide- or *o*-cresotide-chloroform (*Anschtütz*, Ann. 273, 90; 439, 8; *Einhorn*, Ber. 35, 3644).

5-Methyl-*m*-hydroxy-benzoic acid, obtained synthetically by the action of baryta on acetone-oxalic ester (*Claisen*, Ber. 22, 3271), gives, on nitration, 2,4,6-trinitro-*m*'-hydroxy-*m*-toluic acid, or *nitrococcic acid*, m.p.  $180^\circ$ . This is an oxidation product of *carminic acid*, the colouring matter of cochineal (*Miller*, Ber. 26, 2648). 6-Methyl-*m*-hydroxy-benzoic acid is best prepared by heating  $\beta$ -naphthol-6,8-disulphonic acid (p. 625), with 50% sodium hydroxide at  $260$ – $280^\circ$  (*Zincke*, Ann. 350, 253). The three cresotic acids, or better their dibromoderivatives, when treated with sodium and amyl alcohol, open the ring and are reduced to  $\alpha$ -,  $\beta$ -, and  $\gamma$ -methyl-pimelic acids (p. 32) (*Einhorn*, Ann. 295, 193).

Several of these hydroxy-toluic acids have been used in the syntheses of terpenes and terpene-alcohols (Vol. II, p. 221).

*o*-Hydroxy-mesitylenic acid,  $(\text{HO})\text{C}_6\text{H}_2[3,5](\text{CH}_3)_2\text{COOH}$ , m.p.  $179^\circ$  (Jacobson, Ann. 206, 197), has been obtained by nuclear synthesis by condensing  $\alpha$ -methyl- $\beta$ -ethyl-acrolein with malonic ester, and treating the product with sodium ethoxide (p. 26) (Meerwein, Ann. 358, 71):



*p*-Hydroxy-mesitylenic acid, m.p.  $223^\circ$  (Thiele, Ann. 311, 372).

Trimethyl-hydroxy-benzoic acids (Krohn, Ber. 21, 884) and ethyl-methyl-hydroxy-benzoic acids (Jacobsen, Ann. 195, 284) have also been prepared. Two isopropyl-hydroxy-benzoic acids, thymic acid, m.p.  $142^\circ$ , and isohydroxy-cuminic acid, m.p.  $94^\circ$ , are obtained from thymol and carvacrol, respectively, by fusing them with potash. Two *p*-methyl-isopropyl-hydroxy-benzoic acids,  $(\text{CH}_3)(\text{C}_3\text{H}_7)\text{C}_6\text{H}_2(\text{OH})\text{COOH}$ , thymotinic and carvacrotinic acid, have been obtained from thymol and carvacrol, respectively, by introducing  $\text{CO}_2$ . A number of derivatives of thymotinic acid have been described (Heyl, Ber. 28, 2795).

**MONOHYDROXY-PHENYL-FATTY ACIDS.** The analogues of monohydroxy-phenyl-fatty acids, the monohydroxy-phenyl-fatty acids, are obtained (1) from aminophenyl-fatty acids, by diazotising and decomposing the diazo-compound with boiling water; (2) from hydroxy-benzyl cyanides by hydrolysis. *o*-Hydroxy-acids with a phenolic hydroxyl group in the  $\gamma$ - or  $\delta$ -position to the carboxyl group can exist (though the corresponding *o*-amino-acids cannot, p. 329), but they lose water when heated and form  $\gamma$ - and  $\delta$ -lactones (cf. Vol. I, p. 424).

**HYDROXYPHENYL-ACETIC ACIDS**,  $\text{HO}\cdot\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$ , *o*- m.p.  $147^\circ$ , *m*- m.p.  $129^\circ$ , and *p*- m.p.  $148^\circ$ , are isomeric with the ten hydroxy-toluic acids (p. 363), the three methoxy- and the three hydroxymethyl-benzoic acids, and with mandelic acid. The ortho-isomer is closely related to oxindole (p. 330) and isatin (p. 424) and is formed by the reduction of *o*-methoxy-mandelic nitrile, or *o*-hydroxy-mandelic acid with hydriodic acid. It is also formed when coumarone, or  $\alpha$ -chloro-coumarone is acted upon with alcoholic potash, or when  $\alpha$ -nitro-coumarone is reduced with tin and hydrochloric acid (Stoermer, Ber. 34, 1806; 35, 1640; Czaplinski, Ber. 42, 828). It gives a violet colour with ferric chloride. When heated it gives a lactone. The *p*-isomer is found in urine, and is a decomposition product of proteins, and of sinalbin, occurring in white mustard seed (Salkowsky, Ber. 22, 2137).

*o*-, *m*-, *p*-Hydroxy-phenyl-acetic acid, m.p.  $147^\circ$ ,  $129^\circ$ , and  $148^\circ$ , respectively. *p*-Methoxyphenyl-acetic acid, homoanisic acid, m.p.  $86^\circ$ , has been prepared by the action of carbon dioxide on *p*-methoxyphenyl magnesium bromide (Mel-drum, Indian J. 7, 887, 893), and by oxidation of chavicol-methyl ether with permanganate. *m*- and *p*-Hydroxyphenyl-acetonitriles, m.p.  $52^\circ$  and  $69^\circ$  (Solkowsky, Ber. 22, 2139). 5,2-Nitro-hydroxyphenyl-acetic acid,  $\text{C}_6\text{H}_3[5]\text{NO}_2[2](\text{OH})\text{CH}_2\text{COOH}$ , m.p.  $149^\circ$ , has been synthesised by condensing nitro-malonaldehyde with laevulinic acid (p. 25) (Hill, Am. Ch. J. 24, 15). *o*-Mercapto-phenyl-acetic acid,  $\text{HS}[2]\text{C}_6\text{H}_4[1]\text{CH}_2\text{COOH}$ , m.p.  $96\text{--}97^\circ$ , is obtained from *o*-diazophenyl-acetic acid; when distilled it loses water, and is converted into 2-oxy-

thionaphthene,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{CO}$  (Marschalk, Ber. 45, 1484).

**HYDROXYPHENYL-PROPIONIC ACIDS.** Four of the six possible hydroxyphenyl-propionic acids are known. *p*-Hydroxy-hydratropic acid,  $\text{HO}\cdot[4]\text{C}_6\text{H}_4[1]\text{CH}(\text{CH}_3)(\text{COOH})$ , m.p.  $129^\circ$ , is obtained from *p*-amino-hydratropic acid, and from *p*-methoxy-hydratropic acid, the oxidation product of *p*-methoxy-hydratropaldehyde (p. 347). It was formerly thought to be identical with phloretic acid, but it has now been shown that the latter is *p*-hydrocoumaric acid (see below) (Bougault, C.r. 131, 270; 132, 976; Ann. ch. ph. [7], 25, 483; Ciamician, Ber. 27, 1631, 2686).

**HYDROCOUMARIC ACIDS.**  $\beta$ -phenol-propionic acids,  $\text{HO}\cdot\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{COOH}$ ,

COOH, are obtained by reducing the corresponding coumaric acids (hydroxycinnamic or  $\beta$ -hydroxyphenyl-acrylic acids) with sodium amalgam.

***o*-Hydrocoumaric acid**, mellilotic acid, m.p. 82–83°, occurs in *Melilotus officinalis*, partly in the free state, and partly combined with coumarin (*o*-hydroxycinnamic lactone). It can be obtained from the latter by reduction. It gives a faint blue coloration with ferric chloride. Its lactone, hydrocoumarin, is formed when the acid is heated, or treated with thionyl chloride, or dissolved in hydrobromic acid saturated at 0° (*Lasch*, Mo. 34, 1633). When fused with potash it gives salicylic acid. Its sodium and potassium salts, anhydride, amide, and ethyl ester have a biting taste (*Marui*, Tohoku Rep. 17, 695).

***m*-Hydrocoumaric acid**, m.p. 111°, loses water when heated and is converted into *hydroxy- $\alpha$ -hydrindone*,  $\text{HO} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CH}_2$  (*Knake*, Ber. 49, 2103).

***p*-Hydrocoumaric acid**, m.p. 129°, is obtained with phloroglucinol, by decomposing *phloretin*, phloroglucinol compound of *p*-hydrocoumaric acid (C. 1927, II, 54), m.p. 254°, with potash. It is also found in decaying tyrosine, and can be prepared by electrochemical oxidation of hydrocinnamic acid (*Fichter*, C. 1927, II, 54).

$\gamma$ - and  $\delta$ -LACTONES OF HYDROXYPHENYL-FATTY ACIDS. These compounds are formed when the acids are distilled, and correspond to the  $\gamma$ - and  $\delta$ -lactams, described on p. 330.

***o*-Hydroxyphenyl-acetic lactone**,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2\text{CO}[1] \\ \diagup \quad \diagdown \\ \text{O}[2] \end{array}$ , m.p. 49° (unstable form m.p. 28°), b.p. 248–252°, gives  $\alpha$ -chlorocoumarone when treated with phosphorus pentachloride (*Stoermer*, Ann. 313, 84). **Hydrocoumarin**,  $\beta$ -*o*-hydroxyphenyl-propionic lactone,  $\text{C}_6\text{H}_4 \begin{array}{c} [1]\text{CH}_2\text{CH}_2\text{CO} \\ \diagup \quad \diagdown \\ [2]\text{O} \end{array}$ , m.p. 25°, b.p. 272°, is obtained by distillation of the acid, and is reconverted into it when boiled with water. For hydrocoumarin derivatives, see Ger. Pat. 355,650.

### (B) Dihydroxy-monocarboxylic Acids

These are obtained by the same methods as the monohydroxy-carboxylic acids. The carboxyl group is taken up more readily by dihydroxy-benzenes than by the phenols, mere heating to 100–130° with aqueous ammonium or potassium carbonate being sufficient. *m*-Dihydroxy-benzenes react particularly readily (*Kostanecki*, Ber. 18, 3202; 19, 2318; *Brunner*, Ann. 351, 313). The dihydroxybenzoic acids decompose on heating into carbon dioxide and dihydroxy-benzenes. For the action of boiling water on dihydroxybenzoic acids and their bromo- and nitro-derivatives, see *Hemmelmayr*, Mo. 33, 971.

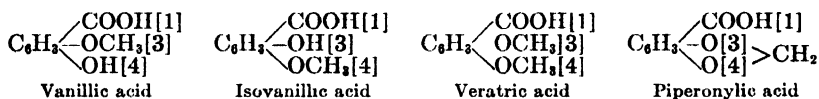
**DIHYDROXY-BENZOIC ACIDS.** The six possible isomers are known. The most important of them is **protocatechuic acid**, 3,4-dihydroxybenzoic acid,  $(\text{HO})_2[3,4]\text{C}_6\text{H}_3[1]\text{COOH} + \text{H}_2\text{O}$ , yellow needles, m.p. 199° (anhydrous) (*Massol*, Bull. [3], 23, 331) with decomp. into pyrocatechol and carbon dioxide. It occurs in the fruit of various species of *Illicium*, and in other plants. Many tri-derivatives of benzene with radicals in the 3,4-positions relative to the side-chain give protocatechuic acid when fused with potash; thus, bromo- and iodo-*p*-hydroxybenzoic acids, *p*- and *m*-cresol-sulphonic acids, sulpho-*p*- and sulpho-*m*-hydroxybenzoic acids, eugenol, piperic acid (cf. piperonylic acid, below), and other substances give this reaction. Derivatives of poly-hydroxyflavones, such as luteolin, fisetin,

quercetin, etc., and of polyhydroxybenzophenones, such as maclurin (Vol. II, p. 451), various resins (e.g., benzoin, asafoetida, myrrh, and particularly kino, from which it can readily be obtained in quantity) also give protocatechuic acid when fused with potash or soda (*Stenhouse*, Ann. 177, 188). See also the phloroglucinol protocatechuates.

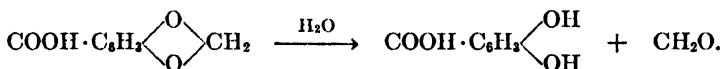
It is also formed by the action of bromine on an aqueous solution of quinic acid. When pyrocatechol is heated to 140° with aqueous ammonium carbonate, the two possible pyrocatechol-monocarboxylic acids are formed.

A solution of protocatechuic acid gives a green coloration with ferric chloride; if then a very dilute solution of sodium carbonate or ammonia is added, the colour becomes blue, and finally red. This reaction is common to all compounds containing the protocatechuic radical,  $(\text{OH})_2\text{C}_6\text{H}_3\text{C}$  (*Tiemann*, Ber. 14, 956). The acid reduces ammoniacal silver nitrate, but not Fehling's solution. When boiled with arsenic acid, *di-protocatechuic acid*,  $\text{C}_{14}\text{H}_{10}\text{O}_7$ , is formed. This compound is a depside, which gives a green coloration with ferric chloride. It combines in equivalent proportions with *p*-hydroxybenzoic acid (*Hlasiwicz*, Ann. 134, 278). Its derivatives are oxidised by nitric acid to derivatives of  $\beta$ -naphthoquinone.

The following phenol-ethers of protocatechuic acid are known:



These alkyl- and alkylene ether-acids are formed by the action of methyl iodide, methylene iodide, and ethylene dibromide on protocatechuic acid in the presence of potash, and by the oxidation of protocatechu-aldehyde. With hydrochloric acid at 150° protocatechuic acid is re-formed from the dimethyl-ether acid, with the intermediate formation of the two monomethyl-ether acids. Under the same conditions, the methylene ether gives piperonylic acid and formaldehyde:



Part of the formaldehyde condenses with the phenolic hydroxyl groups and dark-coloured polymeric products are formed (*Parys*, Rec. 49, 17). The alkyl-ether-acids are decomposed when heated with lime or baryta, carbon dioxide being eliminated and pyrocatechol-alkyl ethers formed.

**Vanillic acid**, 3-methoxy-4-hydroxybenzoic acid, m.p. 211° (sublimes), is obtained by vigorous oxidation of its aldehyde, vanillin (p. 347), and therefore also by the oxidation of coniferin, and by hydrolysis of *aceto-vanillic acid*, m.p. 142°; the latter is obtained by oxidation of acet-eugenol, aceto-ferulic acid, and aceto-homovanillic acid with permanganate. Nitrile, m.p. 89°.

**Isovanillic acid**, 3-hydroxy-4-methoxy-benzoic acid, m.p. 250°, was first obtained by heating hemipinic acid, a 4,5-dimethoxy-*o*-phthalic acid (p. 359), with hydrochloric acid.

**Veratric acid**, 3,4-dimethoxy-benzoic acid, m.p. 179°, occurs in the seeds of *Veratrum sabadilla*, together with an alkaloid, *veratrine*. *m*-Methyl-*p*-ethyl-ether-protocatechuic acid, *m*-methoxy-*p*-ethoxy-benzoic acid, m.p. 195–196°, is obtained from iso-eugenol-ethyl ether. **Diethoxy-benzoic acid**, m.p. 149°.

**Piperonylic acid**, methylene-dioxy-benzoic acid, m.p. 230°, can be obtained by oxidising  $\alpha$ -homopiperonylic acid (p. 365), which is itself the first oxidation product of safrol, and also from piperonal (*Schriner*, Org. Synth. 10, 82), and from protocatechuic acid (p. 365). For its decomposition when heated with hydrochloric acid, see above. When acted upon by phosphorus pentachloride, followed by cold water, it is converted into protocatechuic carbonate, and when this is hydrolysed, the acid itself is formed (*Burger*, J. 93, 563). This is a reaction similar to that occurring when piperonal is converted into protocatechu-aldehyde

(p. 349). Nitrile, m.p. 95° (Marcus, Ber. 24, 3656). Ethylene-dihydroxybenzoic acid, m.p. 133°.

*Proteic acid*,  $C_6H_{10}O_4$ , m.p. 187°, occurs in *Protea mellifera*, and appears to be an ethyl-protocatechuic acid (Hesse, Ann. 290, 319).

*Pyrocatechol-o-carboxylic acid*, 2,3-dihydroxybenzoic acid,  $(HO)_2C_6H_3COOH + 2H_2O$ , m.p. 199° (anhyd.), decomposes readily into carbon dioxide and pyrocatechol, and is formed, together with protocatechuic acid, by the action of ammonium carbonate or potassium bicarbonate on pyrocatechol (Brunner, Ann. 351, 320; Praxmarer, Mo. 27, 1199). It is also formed when 3-iodo-salicylic acid is fused with potash. Its 3-methyl-ether acid, m.p. 148°, is obtained from its aldehyde, *o*-vanillin, by oxidation, the OH-group being temporarily protected (Arch. Pharm. 253, 33). The methyl ester of this acid occurs in the essential oil of primrose root, together with the isomer, the so-called primula-camphor (see below) (Goris, Bull. Pharm. 1912). 2,3-Dimethoxybenzoic acid, *o*-veratric acid, m.p. 122°, is obtained by oxidising either *o*-eugenol methyl ether, or *o*-veratraldehyde (Perkin, Robinson, J. 105, 2376).

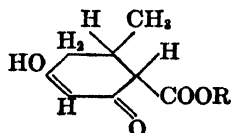
**RESORCINOL-MONOCARBOXYLIC ACIDS.** There are three isomers; the symmetrical dihydroxybenzoic acid is obtained from *sym*-disulphobenzoic acid (p. 334) by fusion with potash, and the two others from resorcinol by the action of aqueous ammonium carbonate or potassium bicarbonate (Tiemann, Ber. 13, 2379; Bistrzycki, Ber. 18, 1985; Brunner, Ann. 351, 320; Shriner, Org. Synth. 10, 95). The  $\alpha$ -compound gives no colour with ferric chloride, the  $\beta$ -acid gives a dark red colour, and the  $\gamma$ -acid a bluish-violet colour.

$\alpha$ -Resorcylic acid, 3,5-dihydroxybenzoic acid,  $(HO)_2C_6H_3COOH + 1\frac{1}{2}H_2O$ , m.p. 233°, gives anthrachryson when treated with hot sulphuric acid.  $\beta$ -Resorcylic acid, 2,4-dihydroxybenzoic acid,  $(HO)_2C_6H_3COOH + 3H_2O$ , m.p. 213° (anhyd.). The ethers and esters of this acid have been described by Perkin (J. 67, 990; Proc. 19, 14; Gregor, Mo. 16, 1881). With chlorine in acetic acid, it gives hexachloro-*m*-diketo-tetrahydrobenzene (Vol. II, p. 117) (Zincke, Ber. 25, 2687). Nitrile, m.p. 175°. The methyl ester of its 4-methyl-ether acid, *primula-camphor*, m.p. 158–159°, occurs in the essential oil of primrose root (Goris, Bull. Pharm. 1912). The dimethyl-ether acid, m.p. 186–187° (Mauthner, J. pr. 121, 264).  $\gamma$ -Resorcylic acid, 2,6-dihydroxybenzoic acid, melts between 148° and 167°, with decomposition into resorcinol and carbon dioxide.

*Gentisic acid*, hydroquinone-carboxylic acid, 2,5-dihydroxybenzoic acid, m.p. 200°, decomposes at 215°. It was first obtained from *gentisin*, a xanthone derivative, by fusion with potash. Phloroglucinol is formed simultaneously. It is obtained from hydroquinone and gentisic aldehyde (p. 350) (Ber. 14, 1988), and from 5-bromo-, 5-iodo-, and 5-amino-salicylic acids. The best method of preparation is to oxidise salicylic acid in alkaline solution with potassium persulphate (Graebe, Ann. 340, 213; Fichter, Helv. 3, 22; Neubauer, Z. physiol. Chem. 52, 375). It gives a deep blue colour with ferric chloride, and is decomposed by this reagent into quinone and carbon dioxide (Nef, Ber. 18, 3499). For *O*-benzoyl derivatives of  $\beta$ -resorcylic acid and gentisic acid, see Bergmann, Ber. 52, 371.

**DIHYDROXY-TOLUIC ACIDS**,  $(HO)_2C_6H_2(CH_3)COOH$ , are isomeric with dihydroxy-phenylacetic acids. A number of acids, methyl ethers, and diesters (Vol. II, p. 381) belonging to this group have been detected in lichens (*Asahina*, Ber. 65, 175).

*Orsellinic acid*, 4,6-dihydroxy-*o*-toluic acid (Henrich, Ber. 37, 1406; Fischer, Ann. 391, 349), m.p. 176°, with decomp. into carbon dioxide and orcinol (p. 230), is obtained from orsellinic acid (see below) by boiling with water, from erythrin by the action of baryta water, from orsellaldehyde (p. 350) by oxidation, and synthetically from crotonic and acetoacetic esters, which condense under the action of sodium ethoxide to give the so-called dihydro-orsellinic ester



This is treated with bromine to remove 2H, and then with catalytically activated hydrogen to remove any bromine from the ring (Sonn, Ber. 61, 926). It gives a



violet colour with ferric chloride. Its 4-methyl ether, *everninic acid*, m.p. 169° (decomp.), is obtained, together with orsellinic acid, by boiling the dipeptide, *evernic acid* (see below) with baryta. It is probably present in extract of *Lichen plicatus* (Walbaum, Ber. 57, 770). It gives a red colour with ferric chloride. Its methyl ester, *sparassol*,  $\text{CH}_3\text{O}[4]\text{HO}[6]\text{CH}_2[2]\text{C}_6\text{H}_3[1]\text{COOCH}_3$ , m.p. 67–68°, is produced in the metabolism of the fungus *Sparassis racemosa* (Wedekind, Ber. 57, 1121).

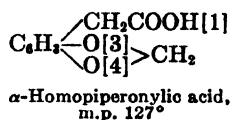
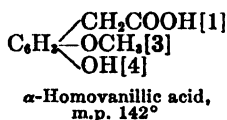
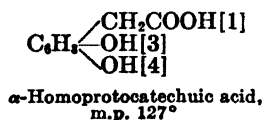
**Orsellic acid, diorsellinic acid, or lecanoric acid**,  $\text{C}_{10}\text{H}_{10}\text{O}_7$ , m.p. 166°, is the dipeptide of orsellinic acid  $(\text{HO})_2[4,6]\text{CH}_2[2]\text{C}_6\text{H}_3[1]\cdot\text{O}[4']\text{C}_6\text{H}_3[6']\text{OH}[2']\cdot\text{CH}_2[1']\text{COOH}$  (Fischer, Ber. 46, 1138). It occurs in a number of lichens of the genera *Rocella*, *Parmella*, and *Lecanora*. It gives a red colour with ferric chloride, and when boiled with water is converted into orsellinic acid. Its 4-methyl ether, *evernic acid*, m.p. 168–169°. *Gyrophoric acid*, m.p. 220° (decomp.) is a tripeptide of orsellic acid and occurs in *Gyrophora esculenta* (Asahina, Ber. 63, 3044). These depsides, and also *erythrin*, erythritol orsellate, are more fully described in connection with tannins, Vol. II, p. 382.

**p-Orsellinic acid, 2,6-dihydroxy-p-toluic acid**, m.p. 178–179°, is prepared as follows: atranorin, from the lichen *Lecanora atra* (see below), is treated with hot acetic acid, and the resulting mixture is extracted with sodium carbonate solution. *Atranol*, p-oryl-aldehyde (p. 350) is soluble in this solution. The aldehyde is then oxidised to p-orsellinic acid. An alcoholic solution of the acid gives a green colour with ferric chloride (Pfau, Helv. 9, 650).

**DIHYDROXY-XYLIC ACIDS.** The methyl ester of  $\beta$ -orcinol-carboxylic acid, *atraric acid, physcianin*,  $(\text{HO})_2[2,4](\text{CH}_2)_2[3,6]\text{C}_6\text{HCOOCH}_3$ , m.p. 142°, is found in the oil from the lichen *Evernia prunastri* and in lichens of the genus *Physcia*. Its dipeptide, *atranorin*, is a constituent of many lichens. It gives atraric acid when heated to 150° with water or alcohol. The 4-methyl ether, m.p. 94°, is obtained by methylating it with diazomethane (Pfau, Helv. 11, 864; Sohn, Ber. 62, 3012).

**Dihydroxy-durylic acid**,  $(\text{HO})_2[2,5]\text{C}_6[3,4,6](\text{CH}_2)_3\text{COOH}$ , m.p. 210° on rapid heating, is the reduction product of durylic quinone, *pseudocumonoquinone-carboxylic acid*,  $\text{O}_2[2,5]\text{C}_6[3,4,6](\text{CH}_2)_3\text{COOH}$ , decomp. at 130°, obtained by the action of ferric chloride on a hydrochloric acid solution of diamino-durylic acid (Nef, Ann. 237, 11).

**DIHYDROXY-PHENYL-FATTY ACIDS.** Certain dihydroxyphenyl-acetic and -propionic acids are of interest. In  $\alpha$ -homoprotocatechuic acid, and its ether-acids, the substituting groups occupy the same positions as in protocatechuic acid and its ether acids:



$\alpha$ -Homopiperonylic acid is prepared by careful oxidation of safrol (p. 452) with permanganate. Under the same conditions aceto- $\alpha$ -homovanillic acid is obtained from aceto-eugenol. The latter acid, m.p. 140°, gives  $\alpha$ -homovanillic acid when hydrolysed with caustic soda, and when this is treated with hydrochloric acid at 180°,  $\alpha$ -homoprotocatechuic acid is formed (Tiemann, Ber. 10, 207; 24, 2882).  $\alpha$ -Homovanillic acid has also been obtained from vanillin and hippuric acid, which condense to a so-called azlactone (p. 267). This is converted into its pyruvic derivative, and then oxidised with hydrogen peroxide (p. 289). Similarly, piperonal gives  $\alpha$ -homopiperonylic acid (Mauthner, Ann. 370, 372).  $\alpha$ -Homoprotocatechuic acid is best prepared by boiling the cyanhydrin of O-methyl-vanillin with hydriodic acid (Piclet, Ber. 42, 2949). Piperonal cyanhydrin has been converted, through its imido-ether, into the corresponding mandelic ester; this has been chlorinated in the  $\alpha$ -position, and then reduced, when homopiperonylic ester is formed (Slotta, J. pr. 139, 211). Homoveratric acid,  $(\text{CH}_3\text{O})_2[3,4]\text{C}_6\text{H}_2[1]\text{CH}_2\text{COOH}$ , m.p. 99°.

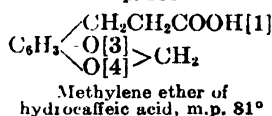
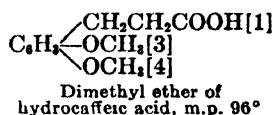
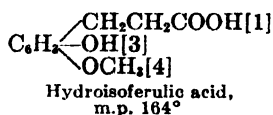
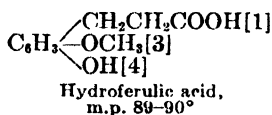
**2-Hydroxy-3-methoxy-phenylacetic acid**, m.p. 124°, is obtained by reducing 2,3-dimethoxy-mandelic nitrile with hydriodic acid. If the action is prolonged,

7-hydroxy- $\alpha$ -coumarone,  $\text{HO}[3]\text{C}_6\text{H}_3\begin{array}{c} \text{CH}_2[1] \\ \diagup \quad \diagdown \\ \text{O}[2] \end{array}\text{CO}$ , m.p.  $189^\circ$  is formed (Mosi-mann, Ber. 49, 1258).

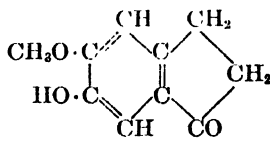
2,5-Dihydroxyphenyl-acetic acid, *homogentisic acid*, m.p.  $147^\circ$ , is found in the urine of patients suffering from alkaptonuria. It crystallises with 1 mol. of water. Syntheses: from 2,5-dimethoxy-phenyl-acetonitrile, obtained by the action of potassium cyanide on dimethoxy-benzyl chloride; from 2,5-dihydroxy-mandelic acid by boiling with hydriodic acid; and from monobenzoyl-hydroquinone-allyl ether, which rearranges to C-allyl-hydroquinone, the dibenzoate of which is oxidised (Neubauer, Z. physiol. Chem. 52, 375; Hahn, *ibid.*, 181, 88).

*sym*-Dihydroxyphenyl-acetic acid,  $(\text{HO})_2[3,5]\text{C}_6\text{H}_3[1]\text{CH}_2\text{COOH} + \text{H}_2\text{O}$ , m.p.  $54^\circ$ , has been obtained by the action of alkalis on dihydroxy-phenyl-acetic-dicarboxylic ester,  $(\text{COOC}_2\text{H}_5)_2\text{C}_6\text{H}_3[3,5](\text{OH})_2[1]\text{CH}_2\text{COOC}_2\text{H}_5$ , m.p.  $98^\circ$ , the condensation product of acetone-dicarboxylic ester when treated with sodium (Pechmann, Ber. 31, 1214; Jerdan, Proc. 1899, 151). Its silver salt gives orcinol on heating.

Hydrocaffeic acid,  $\beta$ -3,4-dihydroxyphenyl-propionic acid, has the same arrangement of substituents as protocatechuic acid and  $\alpha$ -homoprotocatechuic acid:



Hydrocaffeic acid itself, and its derivatives, are obtained from caffeic acid, 3,4-dihydroxy-cinnamic acid, and its derivatives, ferulic and isoferulic acids, by reduction with sodium amalgam (Tiemann, Ber. 11, 650; Lorenz, Ber. 13, 958). The methylene-ether acid is also formed when  $\beta$ -hydropiperinic acid (p. 477) is oxidised (Regel, Ber. 20, 421). Hydrocaffeic acid gives the same colour as protocatechuic acid with ferric chloride (p. 366). When hydroferulic acid is dissolved in sulphuric acid, it is converted into a hydrindone:



m.p.  $193-194^\circ$  (Konek, Ber. 55, 102). Ethyl hydroferulate, b.p.  $193^\circ$  (17 mm.) and the alcohol formed from it by reduction, have bitter tastes (Nomura, Tohoku, 17, 693).

Hydroumbelllic acid,  $\beta$ -2,4-dihydroxyphenyl-propionic acid,  $(\text{HO})_2[2,4]\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{COOH}$ , decomp. at  $110^\circ$ , is prepared by the action of sodium amalgam on umbelliferone, 2,4-dihydroxy-cinnamic- $\delta$ -lactone. It gives a green colour with ferric chloride.

Hydroquinone-propionic acid,  $(\text{HO})_2[2,5]\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{COOH}$ , is obtained in the form of its lactone, m.p.  $163^\circ$ , by oxidising *o*-hydrocoumaric acid in alkaline solution with potassium persulphate (Neubauer, Z. physiol. Chem. 52, 375). Tetrahydropiperinic acid,  $(\text{CH}_2\text{O})_2[3,4]\text{C}_6\text{H}_3\cdot(\text{CH}_2)_4\text{COOH}$ , m.p.  $98^\circ$ , is formed by the catalytic reduction of piperinic, chavicinic (p. 481), and  $\beta$ -hydropiperinic acids (p. 477) (Ott, Ber. 55, 2653).

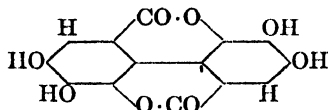
### (C) Trihydroxy-benzoic Acids, $(\text{HO})_3\text{C}_6\text{H}_3\text{COOH}$

Theoretically, six isomers are possible, but only four are known. The most important is

**Gallic acid**,  $(\text{HO})_3[3,4,5]\text{C}_6\text{H}_2\text{COOH} + \text{H}_2\text{O}$ , m.p.  $222^\circ$ , with decomp. into carbon dioxide and pyrogallol. It occurs in the free state in *tea*, *divi-divi*, the fruit of *Caesalpinia coriaria*, pomegranate root, and many other plants. It is obtained by boiling *tannin*, the common tannic acid, with dilute acids. It has been prepared artificially by fusing 4-bromo- $\alpha$ -resorcylic acid, or 5-bromo-catechuic acid, with potash.

Gallic acid crystallises in needles with a silky lustre. It is sparingly soluble in cold water, but dissolves freely in hot water, and in alcohol and ether. It has a stringent, feebly acidic taste. It reduces gold and silver salts and is used for this purpose in photography. Its solution gives a dark blue precipitate with ferric chloride. Its alkali-metal salts absorb oxygen, and turn brown in air.

When heated with sulphuric acid, gallic acid is converted into *rufigallic acid*, a derivative of anthracene. When oxidised with arsenic acid, potassium persulphate, or iodine, or when methyl gallate is boiled with ferric chloride, *ellagic acid*,  $\text{C}_{10}\text{H}_6\text{O}_8$ , is formed. This compound should be regarded as hexahydroxydiphenyl-dicarboxylic dilactone:

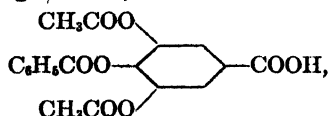


(p. 506; Vol. II, p. 393) (*Nierenstein*, Ann. **394**, 249; *Schwenk*, J. pr. **90**, 53). Ellagic acid is formed, together with its monolactone, *luteic acid*,  $\text{CO}\cdot\text{C}_6\text{H}(\text{OH}_2)$

$\text{O}-\text{C}_6\text{H}(\text{OH})_2\text{COOH}$ , with particular ease, when tannin is oxidised with hydrogen peroxide. When distilled with zinc dust, ellagic acid gives fluorene (p. 678). For its electrolytic reduction, see *Nierenstein*, loc. cit. In alkaline solution, gallic acid changes into *galloflavin*, a yellow dye of the xanthone group. When treated with potassium chlorate and hydrochloric acid, gallic acid is decomposed to isotrachelo-glyceric acid (trichloro-pyroracemic acid) (Vol. I, p. 464). It combines with other aromatic acids to give chains of a depside nature (*Mauthner*, J, pr. **87**, 409).

**Basic bismuth hydroxygallate**,  $(\text{HO})_3\cdot\text{C}_6\text{H}_2\text{CO}_2\text{Bi}(\text{OH})_2$ , known as *dermatol*, is used as an odourless antiseptic in powder form, and **bismuth gallate hydroxyiodide**,  $(\text{HO})_3\text{C}_6\text{H}_2\text{CO}_2\text{Bi}(\text{OH})\text{I}$ , *airol*, is a substitute for iodoform. **Ethyl gallate**,  $(\text{HO})_3\text{C}_6\text{H}_2\text{COOC}_2\text{H}_5$ , m.p.  $141^\circ$  (anhydrous).

**Trimethyl-gallic acid**,  $(\text{CH}_3\text{O})_3\text{C}_6\text{H}_2\text{COOH}$ , m.p.  $170^\circ$ , is a degradation product of podophyllotoxine (Vol. II, p. 492). **Methyl ester**, m.p.  $82-83^\circ$  (*Overmyer*, Am. **49**, 499); **chloride**, m.p.  $77-78^\circ$  (*Bogert*, Am. **36**, 514); **anhydride**, m.p.  $160-161^\circ$  (*Fischer*, Ber. **46**, 1116). **Triethyl-gallic acid**, m.p.  $112^\circ$ . When the trimethoxy-acid is heated with hydrochloric acid, **3,5-dimethyl-gallic acid**,  $\text{HO}[4](\text{CH}_3\text{O})_2[3,5]\text{C}_6\text{H}_2\text{COOH}$ , m.p.  $204^\circ$ , which is identical with *syringic acid* is formed. It is also obtained by oxidation of hydroxy-dimethoxy-cinnamic acid (sinapic acid). For its derivatives see *Bogert*, Am. **37**, 2723). **3-Methyl-gallic acid**, m.p. about  $240^\circ$ , is produced by the hydrolysis of carbonylo-methyl-gallic methyl ester,  $\text{CO}\cdot\text{O}_2[4,5]\text{CH}_2\text{O}[3]\text{C}_6\text{H}_2\text{COOCH}_3$  (*Fischer*, loc. cit.). **4-Methyl-gallic acid**, m.p.  $240^\circ$ , has been prepared by *Graebe* (Ber. **36**, 215, 660) by the action of dimethyl sulphate on gallic acid. **Myristicin acid**,  $(\text{CH}_3\text{O})\cdot(\text{CH}_2\text{O}_2)\cdot\text{C}_6\text{H}_2\text{COOH}$ , m.p.  $210^\circ$ . **Triacetyl-gallic acid**, m.p.  $171^\circ$  (decomp.). **m,m'-Diacetyl-p-benzoyl-gallic acid**,



m.p. 183°, has been studied by *Emil Fischer* (Ber. 51, 45) as an example of intramolecular re-esterification, since by careful hydrolysis it is converted into *m-benzoyl-gallic acid*,  $(C_6H_5COO)(HO)_2 \cdot C_6H_4COOH$ .

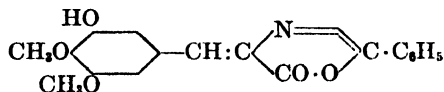
*Gallic anilide*, *gallanol*, and *dibromogallic acid*, *gallobromol*, m.p. 140°, are used in medicine. For other derivatives of gallic acid see *Hamburg*, Mo. 19, 593; *Gnehm*, J. pr. 63, 77.

*Pyrogallol-carboxylic acid*,  $(HO)_3[2,3,4]C_6H_2COOH + \frac{1}{2}H_2O$ , m.p. 220° (anhydrous), sublimes in a stream of carbon dioxide without decomp. It is formed when pyrogallol is boiled with potassium bicarbonate (*Kostanecki*, Ber. 18, 3205). It gives a violet colour with ferric chloride. The *triethyl acid*,  $(C_2H_5O)_3C_6H_2COOH$ , m.p. 105°, is obtained by oxidation of triethyl-daphnetic acid.

*Phloroglucinol-carboxylic acid*,  $(HO)_3[2,4,6]C_6H_2COOH + H_2O$ , decomposes into carbon dioxide and phloroglucinol at about 100°. It is produced by boiling phloroglucinol with potassium carbonate solution (*Will*, Ber. 18, 1323). For its ethers see *Herzig*, Mo. 24, 101.

*Hydroxyhydroquinone-carboxylic acid*,  $(HO)_3[2,3,6]C_6H_2[1]COOH$ , m.p. 217–218° (decomp.), is prepared by boiling hydroxy-hydroquinone with a bicarbonate solution, through which carbon dioxide is passed (*Thiele*, Ber. 34, 2840; *Hemmelmayr*, Mo. 32, 786). *Asaronic acid*, *trimethyl-2,4,5-hydroxyhydroquinone carboxylic acid*, m.p. 144°, can be prepared by oxidising synthetic asaryl aldehyde (p. 350) (*Gattermann*, Ber. 32, 290), or by methylating hydroxy-hydroquinone-carboxylic acid (*Bargellini*, Gazz. 42, II, 351). *Triethyl-hydroxyhydroquinone carboxylic acid*,  $(C_2H_5O)_3[2,4,5]C_6H_2COOH$ , m.p. 134°, is formed from  $\alpha$ - or  $\beta$ -triethyl-aesculetin carboxylic acid by the action of permanganate (*Will*, Ber. 16, 2113).

*Iridic acid*, *dimethyl-homogallic acid*,  $(CH_3O)_2(HO)[3,4,5]C_6H_2CH_2COOH$ , m.p. 118°, is formed, together with formic acid and iretol, by the action of barium hydroxide on irigenin (*de Laire*, Ber. 26, 2015). The acid has been synthesised by *Mauthner* (Ann. 449, 102), starting with 3,4-dimethyl-gallic acid, converting it into its aldehyde, condensing this with hippuric acid to the azlactone:



which gives iridic acid on hydrolysis.

*Methyl-iridic acid*, *trimethyl-homogallic acid*,  $(CH_3O)_3[3,4,5]C_6H_2CH_2COOH$ , m.p. 210°, is an oxidation product of elemicin (p. 451), and has been prepared synthetically from the aldehyde of trimethyl-gallic acid (*Mauthner*, Ber. 41, 3662).

*3,4-Dimethoxy-6-oxyacetic-benzoic acid*, *rissic acid*, m.p. 170°, and *derric acid*,  $(CH_3O)_2[3,4](COOH \cdot CH_2O)[6]C_6H_2[1]CH_2COOH$ , m.p. 262° (decomp.), are decomposition products of rotenone, the active principle of the root of *Derris elliptica*, a papilionacea of S. E. Asia (Vol. II, p. 503). *Rissic acid* loses the ring carboxyl when heated, forming 3,4-dimethoxy-phenoxy-acetic acid (*La Forge*, Am. 53, 3896).

*Digallic acid*, *m-galloyl-gallic acid*, *gallic acid dipeptide*,  $(HO)_3[3,4,5]C_6H_2[1]CO \cdot O[3']C_6H_2[1']COOH[4',5']$  (OH)<sub>2</sub>, m.p. 285° (anhyd.) is formed, together with gallic acid by the hydrolysis of tannin (Vol. II, p. 393). It has been synthesised by coupling tricarbethoxy-gallic chloride with 3,5-dicarbethoxy-gallic acid. A normal coupling reaction first takes place, the chlorine of the acid chloride and the hydrogen of the free *p*-hydroxyl of the acid being eliminated, with the formation of a *p*-dipeptide. Then, when the carbethoxy groups are removed by hydrolysis, the acid residue migrates from the *p*- into the *m*-position. A similar migration has been observed with other dipeptides. The acid precipitates glue (*Fischer*, Ber. 52, 809). The ethyl ester of *pentamethyl-m-galloyl-gallic acid*, m.p. 129–130°, is obtained from trimethyl-galloyl chloride, the methyl ester of 3,4-dimethyl-gallic acid, and sodium hydroxide (*Mauthner*, J. pr. 85, 308). *Penta-acetate*, m.p. 193–194° (*Fischer*, Ber. 46, 1116).

*p-Galloyl-gallic acid*, *p-digallic acid*, undergoes a rearrangement when liberated from its esters (see preceding paragraph), and is unknown in the free state. Its derivatives, in which the five hydroxyls are alkylated or acylated, have been pre-

pared from syringic acid derivatives, and from derivatives of galloyl chloride. The pentamethyl-ether acid, m.p. 221–222°, methyl ester, m.p. 172–173°. Pentaacetyl-ester acid, m.p. 202–203°, methyl ester, m.p. 192–193° (*Fischer*, Ber. 46, 1116; 51, 145).

The tannins derived from gallic acid and its derivatives, and related substances are dealt with in Vol. II, p. 378.

## (2) POLYHYDRIC AROMATIC ALCOHOLS WITH ONE HYDROXYL IN THE SIDE-CHAIN AND THEIR OXIDATION PRODUCTS

### 1. Dihydric and Trihydric Aromatic Alcohols

**XYLYLENE ALCOHOLS**,  $C_6H_4(CH_2OH)_2$ , are obtained from the corresponding xylene chlorides and bromides by boiling with aqueous sodium carbonate; the *o*-compound, **phthalyl alcohol**, can also be prepared by reducing *o*-phthaloyl chloride in acetic acid with an excess of sodium amalgam (*Hessert*, Ber. 12, 646), and *m*-xylene alcohol by electrolytic reduction of isophthalic acid (*Mettler*, Ber. 39, 2936).

1,2-Phthalyl alcohol, m.p. 64°; dichloride, m.p. 55°; dibromide, m.p. 95°.  
1,3-Xylylene alcohol, m.p. 46–47°; dichloride, m.p. 34°; dibromide, m.p. 77°.  
1,4-Xylylene alcohol, m.p. 115–116°; dichloride, m.p. 100°; dibromide, m.p. 144°.

The three chlorides are formed when the xylenes are heated to 150° with phosphorus pentachloride (*Colson*, C.r. 101, 1064), and the bromides by the action of bromine on boiling xylene, or in sunlight (*Schramm*, Ber. 18, 1278). *p*-Xylylene chloride has been prepared from benzene and trioxymethylene with zinc chloride. Dichloromethyl compounds,  $C_6H_4(CH_2Cl)_2$ , are obtained from xylenes by the action of formaldehyde and hydrochloric acid (*Braun*, Ber. 67, 1094); they give tetramethyl-benzenes when reduced with zinc dust and sodium hydroxide.

**Ethers**.—Dialkyl ethers of *p*-xylylene alcohol are obtained from the chloride by the action of methyl- or ethyl alcoholic potash, and are converted into monoalkyl ethers by the action of acetyl chloride in the presence of a trace of zinc chloride. Monomethyl ether, b.p. 152° (16 mm.), monoethyl ether, b.p. 154° (16 mm.) (*Quelet*, C.r. 192, 1391).

***o*-Xylylene oxide**, phthalan,  $C_6H_4(CH_2)_2O$ , b.p. 192°, is a colourless oil, with a strong smell of almonds, obtained by heating *o*-xylene bromide with potash (*Willstätter*, Ber. 40, 965). **Tetrachloro-xylylene oxide**,  $C_6Cl_4(CH_2)_2O$ , m.p. 218° (*Graebe*, Ann. 238, 331).

**XYLYLENE SULPHYDRATES**,  $C_6H_4(CH_2SH)_2$ ; 1,2-, m.p. 46°; 1,3-, an oil, b.p. 157°; 1,4-, m.p. 47°, are formed from xylene bromides by the action of alcoholic potassium hydrosulphide. The 1,2-compound combines with aldehydes and ketones with elimination of water, to form cyclic *mercaptals* and *mercaptols*,  $C_6H_4 \begin{smallmatrix} \diagup S \diagdown \\ \diagdown S \diagup \end{smallmatrix} \begin{smallmatrix} R \\ R \end{smallmatrix}$ , and these, on oxidation, give cyclic sulphones (*Kötz*,

Ber. 33, 729; *Autenrieth*, Ber. 34, 1772; 35, 1388).

***o*-Xylylene sulphide**,  $C_6H_4(CH_2)_2S$ , is an oil smelling like mercaptan, obtained by the action of a concentrated solution of potassium sulphide on *o*-xylylene bromide. **Dixylylene disulphide**,  $[C_6H_4(CH_2)_2S]_2$ , m.p. 234°, is obtained at the same time, but is better prepared from *o*-xylylene bromide and  $C_6H_4(CH_2)_2SNa_2$ . On oxidation, xylylene sulphide gives ***o*-xylylene sulphone**,  $C_6H_4(CH_2)_2SO_2$ , m.p. 152°, and its dimer forms a **disulphone**,  $[C_6H_4(CH_2)_2SO_2]_2$ , and with bromine, a stable dibromide,  $[C_6H_4(CH_2)_2SBr]_2$ , m.p. 111° (*Autenrieth*, Ber. 36, 183).

***o*-Xylylene diamine**,  $C_6H_4[1,2](CH_2NH_2)_2$ , a liquid, is obtained from *o*-xylylene bromide and potassium-phthalimide (*Strassmann*, Ber. 21, 578), and by reduction of phthalazine (p. 374). When its hydrochloride is heated ***o*-xylylene-imine**, *dihydro-iso-indole*,  $C_6H_4(CH_2)_2NH$ , b.p. 213°, is formed. This is also obtained by

the reduction of chloro-phthalazide,  $C_6H_4 \begin{smallmatrix} \diagup CCl \diagdown \\ \diagdown CH \diagup \end{smallmatrix} \begin{smallmatrix} N \\ N \end{smallmatrix}$ ; a number of its derivative have been described (*Fränkel*, Ber. 33, 2808).

Ammonia, on the other hand, converts xylylene bromide first into *bis*-xylylene-ammonium bromide,  $C_6H_4(CH_2)_2N \cdot Br(CH_2)_2C_6H_4$ , and on continued action, *bis*-xylylene-diamine,  $[C_6H_4(CH_2)_2NH]_2$ , m.p.  $80^\circ$ , b.p.  $130$ – $135^\circ$  (12 mm.). Xylylene bromide reacts readily with primary, secondary, and tertiary amines as well. Most primary amines, aliphatic or aromatic, form *N*-alkyl- (or *N*-aryl)-xylylene imines; but when an aromatic amine contains substituents in the *o*-position relative to the  $NH_2$ -group, ring-closure cannot take place on account of *steric hindrance* and di-aryl-xylylene-diamines are formed. With secondary amines, cyclic xylylene-ammonium bromides,  $C_6H_4(CH_2)_2N(RR_1)Br$ , are usually formed, and with tertiary amines, xylylene-diammonium bromides. Xylylene bromide may therefore be used for the characterisation of alkaloids (Scholtz, Ber. 40, 852). Triethyl-phosphine reacts with *o*-xylylene bromide like a tertiary amine, with the formation of *o*-xylylene-ditriethyl-phosphonium bromide (Partheil, Ber. 33, 806). *m*- and *p*-Xylylene bromides never give cyclic compounds with amines, but form diamine-derivatives,  $C_6H_4(CH_2NH_2)_2$  (Halfpaap, Ber. 36, 1672).

Pseudocumenylglycol,  $CH_2[1]C_6H_3[2,4](CH_2OH)_2$ , m.p.  $77^\circ$  (Hiell, Ber. 19, 867). Mesitylene-glycol,  $CH_2[1]C_6H_3[3,5](CH_2OH)_2$ , b.p.  $190^\circ$  (20 mm.).  $\omega_2$ -Diamino-mesitylene,  $CH_2C_6H_3(CH_2NH_2)_2$ , b.p.  $268^\circ$  (Landau, Ber. 25, 3017). Mesitylene-glycerol, *mesicerin*,  $C_6H_3[1,3,5](CH_2OH)_3$ , a viscous liquid (Ber. 16, 2509).

*o*-Di- $\alpha$ -hydroxyethyl-benzene,  $C_6H_4[1,2][CH(OH) \cdot CH_3]_2$ , is a yellow oil, formed by the action of methyl magnesium iodide on *o*-phthalaldehyde. When boiled with dilute hydrochloric acid, it is converted into the oxide, 1,3-dimethyl-phthalan, b.p.  $122^\circ$  (50 mm.) (Nelken, Ber. 41, 986). *p*-Di- $\alpha$ -hydroxyethyl-benzene,  $C_6H_4[CH(OH)CH_3]_2$ , is a liquid, obtained from *p*-diacetyl-benzene (Ingle, Ber. 27, 2527). *o*-, *m*-, and *p*-Di-( $\alpha$ -oxalkyl)-benzenes have been prepared by the action of alkyl-magnesium iodides on phthalaldehydes (Deluchat, C.r. 190, 438).

$\alpha, \alpha$ -Dimethyl-, -diethyl-, and di-isopropyl-*o*-xylylene alcohols,  $HOCH_2 \cdot C_6H_4CR_2OH$ , m.p.  $64^\circ$ ,  $82^\circ$ , and  $108^\circ$ , respectively, are formed by the action of the alkyl magnesium halides on phthalide (p. 376). They readily lose water and become oxides, known as *phthalans* (Ludwig, Ber. 40, 3060).

Hydroxy-*m*-xylenols are often found, together with monohydric phenol-alcohols, among the reaction products of formaldehyde and sodium hydroxide with phenols (Auwers, Ber. 40, 2539), e.g., 2,6-dimethylol-*p*-cresol, hydroxy-mesitylene-glycol,  $HO[1]C_6H_3[4]CH_2[2,6](CH_2OH)_2$ , m.p.  $130.5^\circ$ , from *p*-cresol (Ullmann, Ber. 42, 2539).

*p*-Di- $\beta$ -hydroxyethyl-benzene,  $C_6H_4(CH_2CH_2OH)_2$ , m.p.  $86^\circ$ , obtained from *p*-phenylene-diacetic ester (p. 395) by the method of Bouveault and Blanc gives *p*-divinyl-benzene (p. 447) with caustic potash (C. 1931, II, 427). *p*-Di- $\alpha$ -hydroxyisopropyl-benzene,  $C_6H_4(C \cdot OH[CH_3]_2)_2$ , m.p.  $142$ – $143^\circ$ , obtained by the action of methyl magnesium iodide on methyl terephthalate, similarly gives *p*-di-isopropenyl-benzene, by the action of potassium bisulphate, water being eliminated (Bogert, Am. 41, 1676).

There are nine classes of oxidation products derived from those dihydric aromatic alcohols in which the hydroxyl groups are attached to different side chains, corresponding to the nine classes of derivatives of aliphatic glycols.

## 2. Aldehyde Alcohols

In this group, the reduction products of phthalide, hydrophthalide,  $C_6H_4 \begin{array}{l} \diagup [1]CH_2-O \\ \diagdown [2]CH-OH \end{array}$ , a thick liquid, soluble in water, and of dimethyl-phthalide,

dimethyl-hydrophthalide,  $C_6H_4 \begin{array}{l} \diagup [1]C(CH_3)_2 \\ \diagdown CH(OH) \end{array} O$ , m.p.  $89^\circ$ , should be mentioned

(Kothe, Ann. 249, 61).

Phenol-aldehyde-alcohols are obtained synthetically by the action of formaldehyde and hydrochloric acid on phenol-aldehydes. Thus *o*-hydroxylaldehyde-*p*-benzyl alcohol,  $HO[1]CHO[2]C_6H_3[4]CH_2OH$ , m.p.  $108^\circ$ , is obtained from salicylaldehyde (Stoermer, Ber. 34, 2455). 6-( $\beta$ -Methylaminoethyl)-methyl-vanillin, *lodal*,  $(CH_2O)_3[3,4]C_6H_3[1]CHO[6]CH_2CH_2NHCH_3$ , m.p.  $123$ – $124^\circ$ , is

an oxidation product of laudanosine, and has been prepared synthetically from homoveratrylamine by methylation and formylation. It brings about contraction of the uterus, and has important uses in obstetrics (*Buck, Am. 52, 4119*).

### 3. Aromatic Dialdehydes

The three *phthalic aldehydes*, corresponding to the three phthalic acids, are prepared from xylene tetrachlorides or tetrabromides by the same reaction as that used to convert benzylidene chloride into benzaldehyde (p. 264), by heating with water or potassium oxalate. Their tetra-acetates,  $C_6H_4[CH(OCOCH_3)_2]_2$ , are obtained when the three xylenes are oxidised by a mixture of acetic anhydride and concentrated sulphuric acid, or with chromic acid. The *o*-aldehyde, together with *o*-phthalaldehydic acid (p. 379), is formed by ozonisation of naphthalene in acetic acid (*Seekles, Rec. 42, 706; 43, 93*). Terephthalaldehyde has been prepared from *p*-xylene bromide by the action of lead nitrate (*Wegscheider, Mo. 33, 999*), and from *p*-xylene tetrabromide (*Ruzicka, Helv. 15, 1220*). When *o*-phthalaldehyde is treated with ammonia, and the liquid acidified, an intense dark violet coloration is produced (*Thiele, Ann. 311, 353*). *o*-Xylylene tetrachloride,

or better tetrabromide gives *phthalazine*,  $C_6H_4 \begin{matrix} \diagup CH:N \\ \diagdown CH:N \end{matrix}$ , with hydrazine (*Gabriel, Ber. 28, 1830*).

*o*-Phthalaldehyde, m.p.  $56^\circ$ ; dioxime, see below.

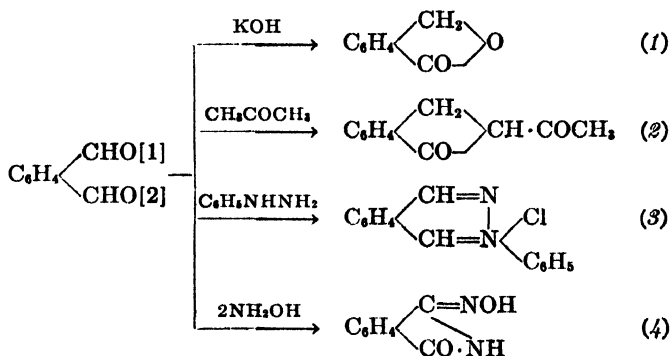
Isophthalaldehyde, m.p.  $89^\circ$ ; dioxime, m.p.  $180^\circ$  (*Thiele, Ann. 347, 109*).

Terephthalaldehyde, m.p.  $116^\circ$ ; dioxime, m.p.  $200^\circ$  (*Kobek, Ber. 16, 2995*).

For the condensation of phthalaldehydes with dimethylaniline, see *Weitz, Ann. 418, 1*. Condensation products of terephthalaldehyde with 2 mols. of aryl-monamines form liquid crystals (*Vorländer*).

*o*-, *m*-, and *p*-Xylylene tetrachlorides,  $C_6H_4(CHCl_2)_2$ , which correspond to the phthalaldehydes, are obtained by heating the xylenes at  $150$ – $190^\circ$  with phosphorus pentachloride: *o*-, m.p.  $89^\circ$ , b.p.  $273^\circ$ ; *m*-, b.p.  $273^\circ$ ; *p*-, m.p.  $93^\circ$ . *o*-, *m*-, and *p*-Xylylene tetrabromides,  $C_6H_4(CHBr)_2$ , m.p.  $116^\circ$ ,  $107^\circ$ , and  $169^\circ$ , respectively, are formed by heating the three xylenes with bromine (*Thiele, Ann. 347, 107*).

*Formation of heterocyclic compounds from o-phthalaldehyde.* (1) Concentrated alkalis give *phthalide*; (2) it condenses with acetone or benzophenone to give  $\beta$ -acetyl- or  $\beta$ -benzoyl-hydrindone; (3) with phenylhydrazine hydrochloride, *phenyl-phthalazonium chloride* is formed; (4) with hydroxylamine, *phthalimidoxime* is formed:



Mesitylene trialdehyde,  $C_6H_3(CHO)_3$ , m.p.  $94^\circ$ , is obtained as a hexacetate by the action of chromic acid and acetic anhydride on mesitylene (*Bielicki, C. 1908, I, 1623*).

**HYDROXY-DIALDEHYDES** are produced by Reimer's reaction (p. 343) to-

gether with, and from, hydroxy-mono-aldehydes. **Thymol-dialdehyde**,  $\text{HO}-\text{C}_6\text{H}(\text{CH}_3)(\text{C}_6\text{H}_7)(\text{CHO})_2$ , m.p.  $79^\circ$ . **Resorcinol-2,4-dialdehyde**,  $(\text{HO})_2\text{C}_6\text{H}_2(\text{CHO})_2$ , m.p.  $127^\circ$  (Tiemann, Ber. 10, 2212; 12, 1003; Baker, J. 1932, 2876).  $\alpha$ - and  $\beta$ -**Orcinol-dialdehydes**,  $(\text{HO})_2\text{C}_6\text{H}(\text{CH}_3)(\text{CHO})_2$ , m.p.  $118^\circ$  and  $168^\circ$  (Tiemann, Ber. 12, 1003).  $\alpha$ - and  $\beta$ -**Hydroxy-isophthalaldehydes**,  $(\text{HO})_2[\text{C}_6\text{H}_3(\text{CHO})_2]$  and  $(\text{HO})_2[2]\text{C}_6\text{H}_2(\text{CHO})_2$ , m.p.  $113^\circ$  and  $125^\circ$ , are obtained by reduction of *p*- and *o*-aldehydo-salicylic acids (Weil, Ber. 55, 301). **4-Hydroxy 5-methoxy-isophthalaldehyde**,  $\text{HO}[4]\text{CH}_2\text{O}[5]\text{C}_6\text{H}_3[1,3](\text{CHO})_2$ , m.p.  $119-121^\circ$ , is obtained, together with vanillin and isovanillin by the action of chloroform and caustic potash on guaiacol. Its methyl ether, m.p.  $124^\circ$ , is obtained by treating it with dimethyl sulphate (Koetschet, Helv. 13, 482). **Hydroxy-uvitic aldehyde**,  $\text{HO}(\text{CH}_2)[2,5]\text{C}_6\text{H}_2[1,3](\text{CHO})_2$ , m.p.  $133^\circ$ , colourless needles, is obtained by oxidising hydroxy-mesitylene glycol (p. 373) (Ullmann, Ber. 42, 2345).

#### 4. di- and tri-Ketones and Hydroxyketones

While only one acyl group can be introduced into benzene by the aluminium chloride synthesis, *p*-**diacetyl-benzene**,  $\text{C}_6\text{H}_4[1,4](\text{COCH}_3)_2$ , m.p.  $114^\circ$ , has been obtained by the action of dilute sulphuric acid on terephthalyl-dimalonic ester (Ingle, Ber. 27, 2527); it has also been obtained by the action of methyl magnesium iodide on terephthalic nitrile (Pfeiffer, Ann. 460, 138), and by ketonic hydrolysis of terephthalyl-bis-acetoacetic ester (Bogert, Ac. Wash. 10, 426). **Diethyl-terephthalyl**,  $\text{C}_6\text{H}_4(\text{COC}_2\text{H}_5)_2$  (?), m.p.  $220^\circ$ . *sym*-**Triacetyl-benzene**,  $\text{C}_6\text{H}_3[1,3,5](\text{COCH}_3)_3$ , m.p.  $163^\circ$ , is formed from formyl-acetone, ring closure occurring with formation of the benzene nucleus.

Benzene homologues, with methyl groups in meta-positions, on the other hand, can readily be converted into ketones by means of aluminium chloride, the acetyl-groups entering between the methyl groups. In this way **durene** and **isodurene** are obtained from mesitylene. **Diacetyl-*m*-xylene**,  $\text{C}_6\text{H}_2(\text{CH}_3)_2(\text{COCH}_3)_2$ , m.p.  $108^\circ$  (Ger. Pat. 515,540); **diacetyl-mesitylene**,  $\text{C}_6\text{H}(\text{CH}_3)_3(\text{COCH}_3)_2$ , m.p.  $46^\circ$ , b.p.  $310^\circ$ ; **diacetyl-durene**, m.p.  $178^\circ$ , b.p.  $323-326^\circ$ ; **diacetyl-isodurene**, m.p.  $121^\circ$ , b.p.  $312-317^\circ$  (Baum, Meyer, Ber. 28, 3213; 29, 1413, 2564).

**2,4-Diacetyl-phenol**,  $\text{C}_6\text{H}_3[1]\text{OH}[2,4](\text{COCH}_3)_2$ , m.p.  $90-91^\circ$ , is prepared from *p*-, or better *o*-acetyl-phenyl acetate, by rearrangement with aluminium chloride (Wittig, J. pr. 130, 81). **Diacetyl-resorcinol**,  $(\text{CH}_3\text{CO})_2[1,5]\text{C}_6\text{H}_2[2,4](\text{OH})_2$ , m.p.  $183^\circ$ , has been obtained by the action of zinc chloride on resorcinol and acetyl chloride (Heller, Ber. 45, 418), and from resorcinol diacetate by the action of ferric chloride, a Fries change occurring (Baker, J. 1934, 71). **1,3-Diacetyl-2,4-dihydroxy-benzene**, m.p.  $177^\circ$  (Wittig, Ann. 446, 184). **Diacetyl-pyrogallol**, *gallo-diacetophenone*,  $\text{C}_6\text{H}(\text{OH})_3[1,2,3](\text{COCH}_3)_2[4,5]$  or  $[4,6]$ , m.p.  $190-191^\circ$ , is formed by heating pyrogallol triacetate with zinc chloride (Heller, Ber. 45, 2391). **Triaceto-phloroglucinol**,  $(\text{CH}_3\text{CO})_3\text{C}_6(\text{OH})_3$ , m.p.  $156^\circ$ , is better regarded as a triketo-cyclohexane derivative (Heller, Ber. 42, 2736; 45, 2389, 2391).

#### 5. Hydroxy-alkyl Carboxylic Acids

**HYDROXYMETHYL-BENZOIC ACIDS**. The three possible isomers have been prepared. They are isomeric with mandelic acid and hydroxy-toluic acids. *o*-Hydroxy-methyl-benzoic acid readily forms a  $\gamma$ -lactone, *phthalide*; this, and meconine, were the first lactones to be prepared.

*o*-Hydroxymethyl-benzoic acid,  $\text{C}_6\text{H}_4 \begin{matrix} \text{COOH}[1] \\ \text{CH}_2\text{OH}[2] \end{matrix}$ , melts at  $120^\circ$

with loss of water and formation of phthalide. It can be re-obtained from the latter by dissolution in aqueous alkali and precipitation with mineral acid. It is also formed from *o*-chloromethyl-benzoic acid by the action of moist silver oxide.



**Phthalide**, *o*-hydroxymethyl-benzoic lactone,  $C_6H_4 \begin{array}{c} \diagup CO[1] \\ \diagdown CH[2] \end{array} O$ ,

m.p. 73–74°, b.p. 290°, was first obtained from *o*-phthalic acid. It is formed: (1) by heating *o*-hydroxymethyl-benzoic acid with water (*Hjelt*, Ber. 25, 528); (2) by reduction of phthalyl chloride with zinc and hydrochloric acid (*Hemers*, Ber. 10, 1443); (3) by reduction of phthalic anhydride with zinc dust and acetic acid, or nickel and hydrogen at 200° (*Wislicenus*, Ber. 17, 2173; *Godchot*, Bull. 1, 829) or under pressure (Ger. Pat. 368,414); (4) by the action of bromine on *o*-toluic acid at 130–140°; and (5) by boiling *sym*-xylylene dichloride with lead nitrate solution. Methods of preparation are: (6) the decomposition of nitroso-phthalimidine (obtained from phthalimide, see below) by caustic potash (*Graebe*, Ann. 247, 291); (7) the action of hydrochloric acid at 100° on *o*-cyanobenzyl chloride in acetic acid (*Cassiver*, Ber. 25, 3021); (8) by heating phthalide-carboxylic acid (p. 439) (*Graebe*, Ber. 31, 394) and (9) by slowly adding phthalimide to a cooled suspension of zinc dust in caustic soda (*Reissert*, Ber. 46, 1489).

Phthalide is oxidised by permanganate to phthalic acid, and reduced by sodium amalgam to hydrophthalide (p. 373), and by hydriodic acid to toluic acid. It combines with benzene in the presence of aluminium chloride, to form *o*-benzyl-benzoic acid, m.p. 114° (p. 522) (*King*, Am. 49, 562); cf. phthal-aldehydo-acid (p. 379), phthalic acid, and *o*-cyano-*o*-toluic acid. Phthalide adds on phenylhydrazine and hydrazine hydrate (Ber. 26, 1273; 33, 766) the lactone ring opening with formation of *o*-hydroxymethylene-benzohydrazide (*Teppema*, Rec. 42, 30).

Many derivatives of *o*-hydroxymethyl-benzoic acid are known, and many readily give heterocyclic compounds, like the parent acid.

*o*-Chloromethyl-benzoic acid,  $ClCH_2[2]C_6H_4[1]COOH$ , m.p. 131°, is formed from phthalide chloride and water, with the loss of hydrogen chloride. Its ethyl ester, b.p. 141° (12 mm.), is obtained similarly from phthalide chloride and ethyl alcohol. Its chloride, **phthalide chloride**,  $ClCH_2[2]C_6H_4COCl$ , b.p. 135° (12 mm.), is formed by the action of phosphorus pentachloride on phthalide at 55–60°, and gives *anthranol* when acted upon by benzene and aluminium chloride. *Amide*,  $ClCH_2[2]C_6H_4CONH_2$ , m.p. 190° (decomp.), is obtained by passing dry ammonia into a solution of phthalide chloride in ether, or by the action of concentrated sulphuric acid on its nitrile. *Anilide*,  $ClCH_2[2]C_6H_4CONHC_6H_5$ , m.p. 115° (*Kiel*, Diss. Bonn. 1896).

*o*-Chloromethyl-benzonitrile,  $Cl \cdot CH_2[2]C_6H_4CN$ , m.p. 252°, is prepared by passing chlorine into boiling *o*-tolunitrile (*Gabriel*, Ber. 20, 2222). The corresponding *o*-cyano-benzyl alcohol,  $HOCH_2C_6H_4CN$ , is not known in the free state, but its ethers have been prepared (*Cassirer*, Ber. 25, 3018).

**Phthalimidine**,  $C_6H_4 \begin{array}{c} \diagup [1]CO \\ \diagdown [2]CH_2 \end{array} NH$ , m.p. 150°, b.p. 337°, is obtained by heat-

ing phthalide in a current of ammonia, by reduction of phthalimide with tin and hydrochloric acid, and by the action of hydrochloric acid on *o*-cyano-benzylamine. **Nitroso-phthalimidine**,  $C_6H_4ON \cdot NO$ , m.p. 156°. **Pseudophthalimidine**,

$C_6H_4 \begin{array}{c} \diagup [1]C=NH \\ \diagdown [2]CH_2 \end{array} O$ , an oil, is formed when *o*-chloro-methyl-benzamide (see above)

is heated at 130–140°, and from phthalide chloride (see above) by the action of alcoholic ammonia. Its hydrochloride decomposes in aqueous solution, even in the cold, into ammonium chloride and phthalide (*Gabriel*, Ber. 32, 2732).

**Phthalide-anil**, **phenyl-phthalimidine**,  $C_6H_4 \begin{array}{c} \diagup [1]CO \\ \diagdown [2]CH_2 \end{array} NC_6H_5$ , m.p. 160°,

is obtained from phthalide and aniline at 200–220°, by reduction of phthalanil with tin and hydrochloric acid, by distillation of *o*-chloromethyl-benzanilide under reduced pressure, and by boiling *o*-cyano-benzylaniline with aqueous potassium carbonate.

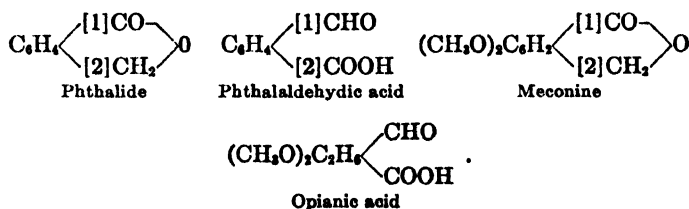
*o*-Cyano-benzylamine,  $\text{NH}_2 \cdot \text{CH}_2[2]\text{C}_6\text{H}_4\text{CN}$ , is a colourless oil, which solidifies to a crystalline mass, and has been obtained by the action of potassium-phthalimide on *o*-cyano-benzyl chloride (*Gabriel*, Ber. 31, 2738). *N*-Diethyl-benzylamine-*o*-carboxylic acid,  $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{C}_6\text{H}_4\text{COOH}$ , m.p. 105° (*Einhorn*, Ann. 300, 163). *o*-Cyano-benzyl-methylamine,  $\text{CNC}_6\text{H}_4\text{CH}_2 \cdot \text{NHCH}_3$ , m.p. 105°; *o*-cyano-benzyl-aniline,  $\text{CNC}_6\text{H}_4\text{CH}_2 \cdot \text{NHC}_6\text{H}_5$ , m.p. 125° (*Fischer*, J. pr. 80, 102).

Thiophthalide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup [1]\text{CO} \\ \diagdown [2]\text{CH}_2 \end{smallmatrix} \text{S}$ , m.p. 60°, and seleno-phthalide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup [1]\text{CO} \\ \diagdown [2]\text{CH}_2 \end{smallmatrix} \text{Se}$ , m.p. 58° (*Graebe*, Ann. 247, 299). Thio-phthalimidine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup [1]\text{CO} \\ \diagdown [2]\text{CH}_2 \\ \diagup \text{CH}_2 \\ \diagdown \text{C}(\text{NH}) \end{smallmatrix} \text{S}$  or *o*-cyano-benzyl-mercaptan,  $\text{C}_6\text{H}_4(\text{CN})\text{CH}_2\text{SH}$ , m.p. 62°, is obtained from *o*-cyano-benzyl-thiocyanate,  $\text{C}_6\text{H}_4(\text{CN})\text{CH}_2\text{SCN}$ , m.p. 86°, by the action of sulphuric acid, and from *o*-cyano-benzyl chloride by the action of potassium hydrosulphide; with an excess of the latter, dithiophthalide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{CS} \end{smallmatrix} \text{S}$ , m.p. 68°, is formed, which easily loses hydrogen sulphide and becomes a stilbene derivative (*Gabriel*, Ber. 31, 2646).

Phthalides substituted in the benzene residue are also known, most of them obtained from substituted *o*-phthalic acids. The following may be mentioned:

*p*-nitrophthalide,  $\text{NO}_2\text{C}_6\text{H}_3 \begin{smallmatrix} \diagup [1]\text{CO} \\ \diagdown [2]\text{CH}_2 \end{smallmatrix} \text{O}$ , m.p. 135°, prepared by oxidising  $\alpha$ -nitro-naphthalene with chromic acid in acetic acid (Ann. 202, 219); *p*-hydroxy-phthalide,  $\text{HO} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup [1]\text{CO} \\ \diagdown [2]\text{CH}_2 \end{smallmatrix} \text{O}$ , m.p. 222° (Ann. 233, 235), from *p*-hydroxy-*o*-phthalic acid. *p*-Amino-phthalide, m.p. 194°, is obtained by the action of zinc dust and caustic soda on *p*-amino-phthalimide; this lactone gives *p*-amino-*o*-hydroxymethyl-benzoic acid when treated with ammonia. The last-named acid has two melting points, 182° and 193° (*Levy, Stephen*, J. 1931, 869, 871).

Meconine, 5,6-dimethoxy-phthalide,  $(\text{CH}_3\text{O})_2[5,6]\text{C}_6\text{H}_2 \begin{smallmatrix} \diagup [1]\text{CO} \\ \diagdown [2]\text{CH}_2 \end{smallmatrix} \text{O}$ , m.p. 102°, is the lactone of *meconinic acid*, which is stable only in the form of its salts. The name is derived from *μῆλον*, poppy. Meconine occurs in opium, in which it was discovered by Couerbe in 1832, and is formed when narcotine is boiled with water (*Wöhler, Liebig*, 1942). It is obtained from its aldehyde-acid, opianic acid (p. 381), in the same way as phthalide from phthalic aldehydo-acid, i.e., by reduction with sodium amalgam, followed by precipitation with an acid. It was the first lactone known.



It was first synthesised by *Fritsch* (Ann. 301, 359), who started with the condensation product of chloral and 2,3-dimethoxybenzoic ester, *dimethoxy-trichloro-*

*methyl-phthalide*,  $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_2\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CHCCl}_2 \end{array}\text{O}$ . When this is treated with alkali, an acid is obtained which yields meconine on heating. *Edwards and Perkin, Jr.* (J. 127, 195) have prepared it from *o*-veratric acid. Potassium cyanide removes the two methoxy-groups from meconine, and two isomeric **hydroxy-methoxy-phthalides** are formed with m.p. 124–125°, and 87–88° (*Rodinow, Ber. 66, 1625*).

**ψ-Meconine**, 3,4-dimethoxy-phthalide,  $(\text{CH}_3\text{O})_2[3,4]\text{C}_6\text{H}_2\begin{array}{c} [1]\text{CO} \\ \diagup \quad \diagdown \\ [2]\text{CH}_2 \end{array}\text{O}$ , m.p. 132°, is obtained from hemipinimide in the same way as phthalide from phthalimide.

**m-Meconine**, 4,5-dimethoxy-phthalide,  $(\text{CH}_3\text{O})_2[4,5]\text{C}_6\text{H}_2\begin{array}{c} [1]\text{CO} \\ \diagup \quad \diagdown \\ [2]\text{CH}_2 \end{array}\text{O}$ , m.p. 155–157°, is prepared by the action of formaldehyde on *m*-veratric acid (*Arch. Pharm. 271, 292*). It gives hemipinic acid, m.p. 203° (decomp.), when treated with permanganate (*Edwards, J. 127, 195*).

**4-Hydroxy-3,5-dimethoxy-phthalide**,  $\text{HO}[4](\text{CH}_3\text{O})_2[3,5]\text{C}_6\text{H}\begin{array}{c} \text{CO}[1] \\ \diagup \quad \diagdown \\ \text{CH}_2[2] \end{array}\text{O}$ , m.p. 144°, and **3,4,5-trimethoxy-phthalide**,  $(\text{CH}_3\text{O})[3,4,5]\text{C}_6\text{H}\begin{array}{c} \text{CO}[1] \\ \diagup \quad \diagdown \\ \text{CH}_2[2] \end{array}\text{O}$ , m.p. 135–136°, are obtained from the corresponding carboxylic acids; the second of the above compounds is also obtained by the condensation of methyl trimethyl-gallate with chloral hydrate in the presence of sulphuric acid, followed by hydrolysis and removal of carbon dioxide (*Bargellini, Lincei 21, II, 146; Alimchandani, J. 117, 964*).

**α-Methyl-phthalide**,  $\text{C}_6\text{H}_4\begin{array}{c} \text{CO}[1] \\ \diagup \quad \diagdown \\ \text{CH}[2] \end{array}\text{O}$ , b.p. 275°, is obtained by reduction of acetophenone-*o*-carboxylic acid (p. 382) with sodium amalgam, and by the action of methyl magnesium iodide on *o*-phthalaldehydic acid (*Simonis, Ber. 38, 3981*). It is reduced by hydriodic acid and phosphorus to *o*-ethyl-benzoic acid. **α-Ethyl-phthalide**, m.p. 12°, b.p. 291°, is prepared in a similar manner (*Giebe, Ber. 29, 2533; Gottlieb, Ber. 32, 960*).

**α,α-Dimethyl-phthalide**,  $\text{C}_6\text{H}_4\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{CH}_3)_2 \end{array}\text{O}$ , m.p. 67°, b.p. 270°, is formed in the action of methyl magnesium iodide on phthalic anhydride (*Bauer, Ber. 37, 735*). **Diethyl, dipropyl, and di-isopropyl-phthalides**, m.p. 54°, 76°, and 84°, are obtained in a similar manner (*Bauer, Arch. Pharm. 247, 220*).

**o-β-Oxyethyl-protocatechuic lactone**,  $\text{C}_6\text{H}_2(\text{OH})_2\begin{array}{c} [1]\text{CO}\cdot\text{O} \\ \diagup \quad \diagdown \\ [2]\text{CH}_2\cdot\text{CH} \end{array}$ , is closely related to a number of alkaloids, such as corydaline, berberine, etc.

**m-Hydroxymethyl-benzoic acid** is only known as the alcoholic anhydride,  $\text{O}[\text{CH}_2[3]\text{C}_6\text{H}_4\text{COOH}]_2$ , m.p. 180°, obtained from *m*-cyano-benzyl chloride,  $\text{Cl}\cdot\text{CH}_2[3]\text{C}_6\text{H}_4\text{CN}$ , m.p. 67°, b.p. 259°. The latter is obtained by the action of chlorine on *m*-tolunitrile. **ω-Chloro-*m*-toluic acid**, m.p. 135°. ***m*-Benzyl-amine-carboxylic acid**,  $\text{NH}_2\cdot\text{CH}_2[3]\text{C}_6\text{H}_4\cdot\text{COOH}$ , m.p. 216°; ***m*-cyano-benzylamine**,  $\text{NH}_2\text{CH}_2[3]\text{C}_6\text{H}_4\text{CN}$  (*Ehrlich, Ber. 34, 3367*).

**p-Hydroxymethyl-benzoic acid**,  $\text{HO}\cdot\text{CH}_2[4]\text{C}_6\text{H}_4\text{COOH}$ , m.p. 181°, is obtained (1) from *p*-bromomethyl-benzoic acid,  $\text{Br}\cdot\text{CH}_2[4]\text{C}_6\text{H}_4\text{COOH}$  (*Dittmar, Ann. 162, 342; Case, Am. 47, 1143*), and (2) from terephthalaldehyde, by the action of concentrated caustic soda (*Loew, Ann. 231, 372*). **p-Cyano-benzyl-alcohol**,  $\text{HOCH}_2[4]\text{C}_6\text{H}_4\text{CN}$ , m.p. 133°, is obtained by the action of potassium carbonate on *p*-cyanobenzyl chloride, m.p. 79°, b.p. 263°. **p-Chloromethyl-benzamide**,  $\text{CH}_2\text{Cl}[4]\text{C}_6\text{H}_4\text{CONH}_2$ , m.p. 173°. **p-Chloromethyl-benzoic acid**,  $\text{CH}_2\text{Cl}[4]\text{C}_6\text{H}_4\text{COOH}$ , m.p. 199° (*Reinglass, Ber. 24, 2416*). For **benzyl-amino-*p*-carboxylic acid**, yellow flakes, **diethyl-benzylamino-*p*-carboxylic acid**, m.p.

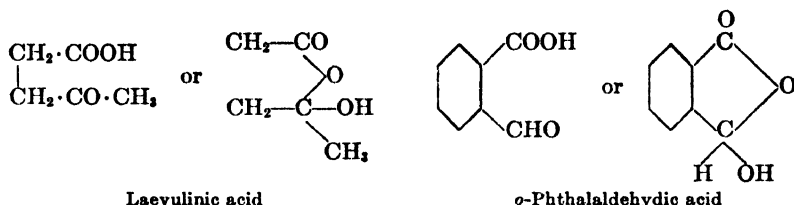
150° (*Günther*, Ber. 23, 1060) and *p*-cyano-benzylamine, see *Einhorn*, Ann. 310, 207, and *Ehrlich*, Ber. 34, 3368.

*p*-Chloromethyl-salicylic acid,  $\text{ClCH}_2[4]\text{C}_6\text{H}_3[1]\text{OH}[2]\text{COOH}$ , m.p. 163°, is obtained from salicylic acid and formaldehyde by the action of hydrochloric acid (Ger. Pat. 121,051).

*m*- and *p*-HYDROXY-ISOPROPYL-BENZOIC ACIDS,  $(\text{CH}_3)_2\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4\text{COOH}$ , m.p. 123° and 155°, are formed when *m*- and *p*-cymenes are oxidised with permanganate (*Wallach*, Ann. 275, 159); the *p*-acid is also obtained from cuminic acid (p. 293). 3-Amino-4-hydroxy-isopropyl-benzoic acid, which is derived from the *p*-acid, condenses with carboxylic anhydrides to give *cumazonic acids*.

## 6. Aldehydic Acids

*o*-Phthalaldehydic acid, and 5,6-dimethoxy-*o*-phthalaldehydic acid, opianic acid, are the most important aromatic aldehydo-carboxylic acids. The aldehydo-group occupies the  $\gamma$ -position to the carboxyl group in these acids, and, like the aliphatic  $\gamma$ -keto-acids (laevulinic acids, Vol. I, p. 477), they form mono-acetyl derivatives. A  $\gamma$ -hydroxy-lactone formula (*Liebermann*, Ber. 19, 765, 2288) is therefore more probable than a carboxylic acid formula. It is a case of ring-chain tautomerism.



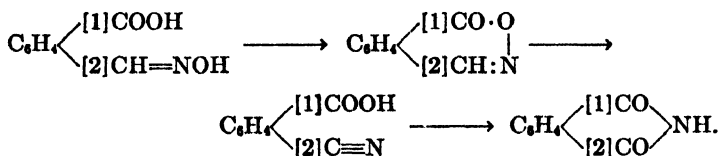
Substituted *o*-aldehydic acids have been prepared from naphthalene derivatives (*Chakravarti*, Indian J. 10, 693). Mono- and di-hydroxy-aldehydic acids have been obtained from mono- and di-hydroxy-carboxylic acids by the action of chloroform and alkali (*Tiemann*, Ber. 12, 1334; *Fürth*, Ber. 16, 2182).

Two series of esters have been prepared from opianic acid. These are regarded as carboxylic, and  $\gamma$ -hydroxylactonic esters, respectively. With methyl alcohol, the methyl ether of hydroxy-phthalide is formed, and with methyl alcohol and a little concentrated sulphuric acid, the normal methyl ester is obtained (*Meyer*, Mo. 25, 497). The  $\psi$ -esters of *o*-phthalaldehydic acid change into normal esters when treated with hydrochloric acid; the  $\psi$ -chloride gives the  $\psi$ -ester on heating with methyl alcohol and potassium carbonate, and the normal oily ester when heated with methyl alcohol alone (*Kirpal*, Ber. 62, 2106).

The behaviour of the oxime-anhydrides of opianic acid and phthalaldehydic acid at higher temperatures is remarkable. They change, with considerable evolution of heat, into phthalimides. In the case of the former compound, *o*-cyano-benzoic acid is formed intermediately, and is converted into phthalimide on fusion. The heats of combustion of opianic oxime anhydride and of hemipinimide have been determined. The heat liberated by the rearrangement of the former into the latter is 52.6 kg.-cal. per g.-mol., which is ten times the molecular energy of rearrangement of allocinnamic acid into cinnamic acid, and eight times that of maleic into fumaric acid (*Liebermann*, Ber. 25, 89).

*o*-Phthalaldehydic acid, m. 100.5°, formula above, is obtained: (1) by heating bromo-phthalide (see below) with water; (2) by heating  $\omega$ -pentachloroxylene, or (3) cyano-benzal chloride with hydrochloric acid (*Gabriel*, Ber. 20, 3197); (4) together with *o*-phthalaldehyde by the ozonisation of naphthalene in acetic acid (*Seekler*, Rec. 43, 329); (5) by heating phthalonic acid, an oxidation product of, naphthalene (p. 440) with an aq. solution of a bisulphite (*Graebe*, Ber. 31, 374) or (6) by converting phthalonic acid into its dianilino-compound. This on heating gives carboxy-benzal-aniline, and by subsequent hydrolysis, *o*-phthalaldehydic

acid; the best methods of preparation are 5 and 6 (*Fuson, Am. 48, 1093*). Phthalaldehydic acid gives: with hydrazine, *phthalazone*,  $C_6H_4 \begin{matrix} [1]CO-NH \\ [2]CH=N \end{matrix}$ , m.p. 184–185°; with phenyl-hydrazine, *phenyl-phthalazone*, m.p. 105° (*Ber. 26, 531*); with potassium cyanide, *phthalide-carboxylic acid*,  $C_6H_4 \begin{matrix} CH \cdot COOH \\ CO \end{matrix}$ , m.p. 150° (*Seekler, loc. cit.*); with hydroxylamine in water, *benzaldoxime-o-carboxylic acid*, m.p. 120°, and in alcohol, *benzaldoxime-o-carboxylic anhydride*, which melts at 145° with rearrangement into *o-cyano-benzoic acid*. In this rearrangement a considerable amount of heat is evolved. At a still higher temperature, the substance changes into phthalimide (*Liebermann, Ber. 26, 3264*).

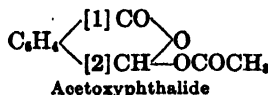
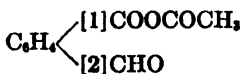
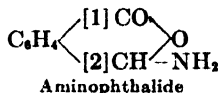
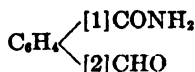
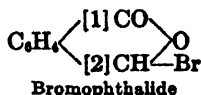
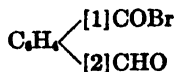
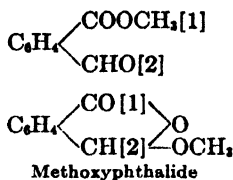


With benzoyl-hydrazine and  $\beta$ -phenyl-hydroxylamine, aldehyde derivatives are the first products (*Bistrzycki, Ber. 34, 1017*). For condensation products with phenols and phenol ethers, see *Brubaker, Am. 49, 2279*.

**Bromo-phthalide**, *phthalaldehydic bromide*, m.p. 85°, produced by the action of bromine vapour on phthalide at 140°, reacts with methyl alcohol to give  $\alpha$ -**methoxy-phthalide**, *methylo-phthalaldehyde*, m.p. 44°, and with ethyl alcohol to give  $\alpha$ -**ethoxy-phthalide**, m.p. 66°. With ammonia, bromo-phthalide gives **amino-phthalide**, *phthalaldehydamide*. **3-Chloro- $\alpha$ -hydroxy-phthalide**,

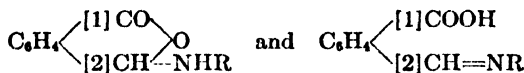
$Cl[3]C_6H_3 \begin{matrix} [1]CO \\ [2]CHOH \end{matrix} O$ , m.p. 138°, has been obtained from 3-chloro-*o*-toluic acid, m.p. 91.5°, by treatment with bromine, followed by heating with dilute sodium acid, hydroxide (*Ulrich, C. 1931, I, 1103*). **Phthalaldehydic-acetic anhydride**, *acetoxo-phthalide*, is prepared by the action of acetic anhydride on

phthalaldehydic acid. **Diphthalide ether**,  $C_6H_4 \begin{matrix} [1]CO \\ [2]CH \end{matrix} O \begin{matrix} O \\ O \end{matrix} \begin{matrix} CO \\ CH \end{matrix} C_6H_4$ , m.p. 221°, is obtained from *o*-phthalaldehydic acid and bromo-phthalide, or by heating it alone at 240–250° (*Graebe, Ber. 31, 371*). Just as phthalaldehydic acid itself can be formulated in two ways (see above), so its derivatives can also be formulated as acids, or as lactones (*pseudo-derivatives*):



The carboxylic anhydride formula is unlikely to be correct for acetoxo-phthalide and diphthalide ether.

Phthalaldehydic acid, and opianic acid, react very readily with amines, even in the cold, water being eliminated. Some of the compounds formed dissolve with difficulty, and others readily in aqueous sodium carbonate. The former are derived from the amino-phthalide formula, and the latter from the imino-aldehydic acid formula (Liebermann, Ber. 29, 174, 2030):

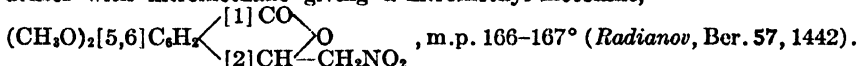


$\alpha$ -Hydroxy-phthalimidine,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CHOH} \\ \diagup \quad \diagdown \\ \text{CO} - \end{array} \text{NH}$ , m.p. 171-172°, is formed by the reduction of phthalimide with zinc dust and sodium hydroxide.

**PHTHALALDEHYDE CHLORIDES.** *o*-Dichloromethyl-benzoic acid,  $\omega$ -dichloro-*o*-toluic acid,  $\text{CHCl}_2[2]\text{C}_6\text{H}_4\text{COOH}$ , m.p. 155°. The chloride of this acid, m.p. 155-157° (28 mm.), is prepared by chlorinating *o*-toluic chloride at 150°, or by treating phthalide with phosphorus pentachloride at 210°. Its amide melts at 180°, turning black, and its anilide at 129° (decomp.) (Kaltwinkel, Diss. Bonn, 1914). *o*-Phthalaldehydic acid pentachloride,  $\omega$ -pentachloro-*o*-xylene,  $\text{CHCl}_2[2]\text{C}_6\text{H}_4\text{CCl}_3$ , m.p. 53°, is formed by the action of phosphorus pentachloride on *o*-xylene at 140°. *o*-Cyano-benzal chloride,  $\text{CHCl}_2[2]\text{C}_6\text{H}_4\text{CN}$ , b.p. 260°, obtained by the action of chlorine on boiling *o*-cyano-toluene, gives first *o*-cyano-benzaldoxime, and then *o*-cyano-benzamide, when treated with hydroxylamine (Braun, Ber. 40, 2709).

Noropianic acid,  $(\text{HO})_2\text{C}_6\text{H}_2(\text{CHO})\text{COOH}$ , m.p. 171°, is formed, together with iso-vanillin and carbon dioxide, when opianic acid is heated with hydriodic acid. It gives a bluish-green colour with ferric chloride.

Opianic acid,  $(\text{CH}_3\text{O})_2[5,6]\text{C}_6\text{H}_2[2](\text{CHO})\text{COOH}$ , m.p. 150°, was discovered by Wöhler and Liebig in 1842 (Ann. 44, 126). They obtained it by oxidising narcotine with manganese dioxide and dilute sulphuric acid. When reduced it gives meconine, and when oxidised, hemipinic acid. When heated with water under pressure (150-200°, 20 atm.), it is converted into isovanillin (Schorigin, Ber. 64, 247). When its solution in caustic potash is evaporated, it is converted partly into meconine and partly into hemipinic acid, a Cannizzaro reaction, like the disproportionation of benzaldehyde to benzyl alcohol and benzoic acid. It condenses with nitromethane giving  $\alpha$ -nitromethyl-meconine,

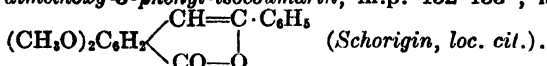


When heated with hydrochloric acid, 5-methoxy-6-hydroxy-phthalaldehydic acid, methyl-noropianic acid,  $(\text{CH}_3\text{O})[5](\text{HO})[6]\text{C}_6\text{H}_2(\text{CHO})\text{COOH}$ , m.p. 155-156° (Liebermann, Ber. 30, 691), is first formed, but loses carbon dioxide giving iso-vanillin. Concentrated sulphuric acid converts opianic acid into rufiopin, a tetrahydroxy-anthraquinone derivative (p. 665).

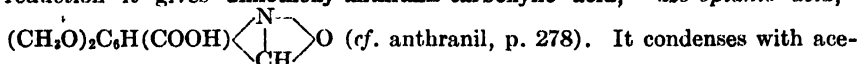
The reactions of opianic acid with hydrazine, phenyl-hydrazine, and hydroxylamine are similar to those of phthalaldehydic acid (p. 379). Dimethoxy-phthalazone, opiazone, m.p. 162° (anhyd.) (Ber. 27, 1418). Phenyl-opiazone, m.p. 175° (Ber. 19, 2518). Opianoximic acid, m.p. 82° becomes opianoximic anhydride, m.p. 114°, simply on boiling with water. When this anhydride is heated alone or boiled in alcoholic solution it is converted into hemipinimide (p. 389) (Allendorff, Ber. 24, 3264).

**Esters.**—There are two series of esters. The true carboxylic esters are stable in water, and give the characteristic reactions of aldehydes. They are formed by the action of alkyl iodides on potassium or silver opianate, by the action of alcohols on opianic chloride, and by the action of diazomethane on opianic acid. The other series,  $\gamma$ -hydroxy-lactonic, or  $\psi$ -esters, are obtained by boiling opianic acid or its chloride, m.p. 94°, with alcohols. Methyl opianate,  $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_2(\text{CHO})\text{COOCH}_3$ , m.p. 82°, b.p. 233° (51 mm.). Ethyl opianate, m.p. 64°. Benzyl opianate, m.p. 82-83°. Methyl  $\psi$ -opianate, m.p. 105°, b.p. 238° (52 mm.). Ethyl  $\psi$ -opianate, m.p. 92°. Benzyl  $\psi$ -opianate, m.p. 94-95° (Wegscheider, Mo. 12, 111; 13, 702; 14, 311; Schorigin, Ber. 64, 1931). On boiling with alcoholic hydrogen chloride, the  $\psi$ -esters are converted into the carboxylic esters (Kirpal,

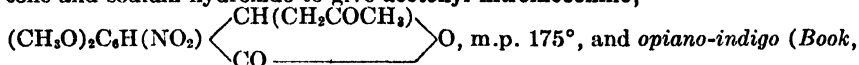
Ber. 60, 382). When normal benzyl opianate in pyridine is heated at 160°, 7,8-dimethoxy-3-phenyl-isocoumarin, m.p. 132-133°, is formed, with ring closure,



**Acetyl-opianic acid**, m.p. 120° (Liebermann, Ber. 19, 2288). **3-Nitro-opianic acid**, m.p. 166°, is most probably a hydroxy-lactone (p. 379), as its affinity constant in aqueous solution is very low (Wegscheider, Ber. 36, 1541); methyl ester, m.p. 78°;  $\psi$ -methyl ester, m.p. 182° (Wegscheider, Mo. 24, 790). On reduction it gives dimethoxy-anthranil-carboxylic acid, "azo-opianic acid,"



It condenses with acetone and sodium hydroxide to give acetonyl-nitromeconine,



**Pseudo-opianic acid**,  $(\text{CH}_3\text{O})_2[3,4]\text{C}_6\text{H}_2[2](\text{CHO})\text{COOH}$ , m.p. 121°, has been prepared by boiling berberal, an oxidation product of the alkaloid berberine, with dilute sulphuric acid; amino-ethyl-piperonyl-carboxylic anhydride is a by-product (Perkin, J. 57, 991). Its oxime, m.p. 124°, undergoes rearrangement into hemipinimide m.p. 228-230°, on heating (Allendorff, Ber. 24, 3266).

**m-Opianic acid**,  $(\text{CH}_3\text{O})_2[4,5]\text{C}_6\text{H}_2[2]\text{CHO}[1]\text{COOH}$ , m.p. 186-187°, is obtained from 3,4-homoveratrol, by converting the latter into 4,5-dimethoxy-*o*-tolyl-methyl ketone, oxidising this to dimethoxy-phthalonic acid, and making the aniline compound of the latter. It can also be obtained from isovanillic acid, by introducing a CHO group by Reimer's method, and partially methylating the product (Fargher, Perkin, J. 119, 1724; 123, 3171). Normal methyl ester, m.p. 93-95°;  $\psi$ -methyl-ester, m.p. 142-143°.

**m-Aldehyde-benzoic acid**, *isophthalaldehydic acid*,  $\text{CHO}[3]\text{C}_6\text{H}_4\text{COOH}$ , m.p. 175°. **m-Cyano-benzaldehyde**, m.p. 80°. **m-Cyano-benzal chloride**, b.p. 274° (Reinglass, Ber. 24, 2416, 2422).

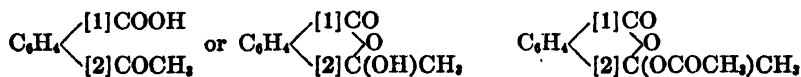
**Isoopianic acid**,  $(\text{CH}_3\text{O})_2[4,5]\text{C}_6\text{H}_2[3]\text{CHO}[1]\text{COOH}$ , m.p. 210-211°, has been prepared by Chakravarti and Perkin, (J. 1929, 193) from vanillic acid by Reimer's method, followed by methylation, and from 5-nitro-  $\longrightarrow$  -amino-  $\longrightarrow$  -cyano-2,3-dimethoxy-cinnamic acid, oxidation to aldehyde, and hydrolysis of the CN group.

**p-Aldehyde-benzoic acid**, terephthalaldehydic acid,  $\text{CHO}[4]\text{C}_6\text{H}_4\text{COOH}$ , m.p. 256°. **p-Cyano-benzaldehyde**, m.p. 97°. **p-Cyano-benzal chloride**, b.p. 275° (Reinglass, Ber. 24, 2422). For the literature of iso- and terephthalaldehydic acids, see Simonis, Ber. 45, 1584.

When anthranilic acid is acted upon by chloroform and caustic potash, an *o*-aminobenzoic aldehydic acid is obtained (Elliott, J. 77, 212).

## 7. Keto-carboxylic Acids

Of the aromatic carboxylic acids containing a keto-group and a carboxyl group in different side chains, the most important is *o*-acetophenone-carboxylic acid. Since the CO and COOH groups are in the  $\gamma$ -position, reactions similar to those of *o*-phthalaldehydic acid are possible (p. 379), and two formulae, one carboxylic and the other  $\gamma$ -lactonic, are equally probable. Its acetyl compound is an acetyl- $\gamma$ -hydroxy-lactone:



***o*-Acetophenone-carboxylic acid**, *o*-acetyl-benzoic acid, m.p. 115°, is isomeric with benzoyl-acetic (p. 429), and with tolyl-glyoxylic (p. 427) acids. It has a sweet taste. It is formed when benzoyl-acetic-*o*-carboxylic acid is boiled with water (Gabriel, Ber. 26, 705; Giebe, Ber. 29, 2533). Acetyl compound, m.p. 70° (Gabriel, Ber. 14, 921). The acid combines with hydrazine to give a methyl-

phthalazone, m.p. 222°, b.p. 247° (*Gabriel*, Ber. 26, 705), with phenylhydrazine to give a methyl-N-phenyl-phthalazone, m.p. 102° (Ber. 18, 803), and with hydroxylamine its ethyl ester gives an oxime anhydride, m.p. 158° (*Gabriel*, Ber. 16, 1995).

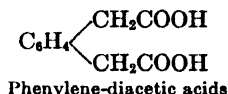
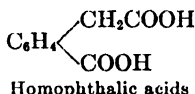
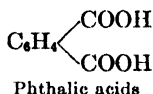
Fatty acids condense with phthalic anhydride with elimination of water and carbon dioxide to form *alkylidene-phthalides*, the anhydrides of *o*-acidyl-benzoic acids, which yield the acids on heating with potash. *o*-Propiophenone-, *o*-butyrophenone, and *o*-isovalerophenone-carboxylic acids, m.p. 92°, 89°, and 88°, have been obtained in this way (Ber. 29, 1437; *Gottlieb*, Ber. 32, 959).

*p*-Acetophenone-carboxylic acid, m.p. 205°, is an oxidation product of *p*-β-hydroxy-isopropyl-benzoic acid (*Meyer*, Ann. 219, 260), and has been prepared by electrolytic oxidation of cymene (*Fichter*, Helv. 8, 285). *p*-Cyano-acetophenone, m.p. 60°, is obtained from *p*-amino-acetophenone.

Methyl-benzyl-ketone-*o*-carboxylic acid, COOH[2]C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>COCH<sub>3</sub>, m.p. 119°, is obtained by boiling methyl-isocoumarin (p. 483) with alkali (*Gottlieb*, Ber. 32, 965). Benzyl-acetone-*o*-carboxylic acid, COOH[2]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>·CH<sub>2</sub>·COCH<sub>3</sub>, m.p. 114° (*Bulow*, Ber. 40, 189).

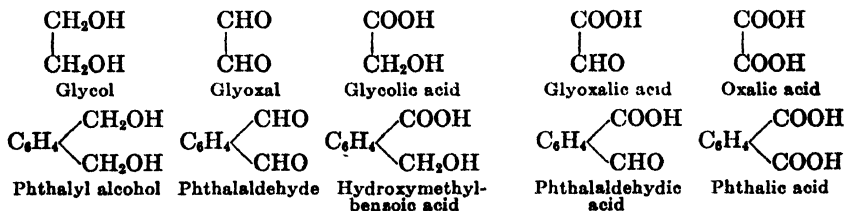
## 8. Polycarboxylic Acids

In each class of these acids, three groups may be distinguished: (a) acids in which all the carboxyl groups are directly attached to the benzene ring; (b) acids with some carboxyl groups in the ring, and others in side-chains; and (c) acids in which all the carboxyl groups are in side-chains; e.g.:



### 1. Dicarboxylic Acids

(a) **PHTHALIC ACIDS.** The phthalic acids are the ultimate oxidation products of all those benzene derivatives which have two side-chains attached to the ring. They are, therefore, extremely important for the determination of the position of such side-chains (p. 9). Their hydrogen addition products, the *hydrophthalic acids* (Vol. II, p. 140) are also theoretically important. As in similar cases, the *o*-acid is distinguished from the *m*- and *p*-compounds by its ability to form an anhydride, and other cyclic compounds; a γ-dihydroxy-lactone formula has been proposed for it, in addition to the dicarboxylic formula (cf. the olefine-dicarboxylic acids, Vol. I, p. 563). *o*-Phthalic acid is of importance industrially as a starting material in the manufacture of phthalein dyestuffs and of anthranilic acid. The relationship between phthalic acids, phthalyl alcohols, phthalaldehydes, hydroxy-methyl-benzoic acids, and phthalic aldehyde acids, is the same as that between oxalic acid, ethylene glycol, glyoxal, glycolic acid, and glyoxalic acid:





**Phthalic acid, benzene-o-dicarboxylic acid,**  $C_6H_4 \begin{matrix} \swarrow [1]COOH \\ \searrow [2]COOH \end{matrix}$  or

$C_6H_4 \begin{matrix} \swarrow C(OH)_2 \\ \searrow O \\ CO \end{matrix}$  (Baeyer, Ann. 269, 155), melts at  $213^\circ$  when rapidly

heated, with decomposition into the anhydride and water. It is produced by the oxidation of naphthalene with nitric acid, permanganate (Ullmann, Ber. 36, 1805), or concentrated sulphuric acid and mercuric sulphate (Ger. Pat. 91,202), the last being the best method. It is manufactured on a large scale. It is obtained, together with benzoic acid by heating naphthols with aqueous sodium hydroxide and copper oxide at  $240-260^\circ$  (Ger. Pat. 139,956), from *o*-xylene, *o*-toluic acid or diphenic acid by oxidation with permanganate or dilute nitric acid, and from alizarin and purpurin by the action of nitric acid, or sulphuric acid and manganese dioxide. Small quantities are formed in the oxidation of benzene and benzoic acids. Chromic acid cannot be used as an oxidising agent in any of the above reactions, as it readily destroys phthalic acid with the formation of carbon dioxide (p. 287). It has been prepared synthetically by converting *o*-nitrobenzoic acid into *o*-cyano-benzoic acid and boiling this with alkali (p. 387).

*History.*—Phthalic acid was first obtained by *Laurent* in 1836, by the oxidation of naphthalene tetrachloride. He regarded it as a naphthalene derivative, and called it naphthalenic acid (Ann. 19, 38). *Marignac* established its correct formula,  $C_8H_6O_4$  (Ann. 38, 13), which showed that it was not a derivative of naphthalene. *Laurent* then called it phthalinic acid (Ann. 41, 107).

When heated with excess potash, phthalic acid decomposes to give benzene and two molecules of carbon dioxide. When one mol. of its calcium salt is heated to  $300-350^\circ$  with one mol. of slaked lime, only one molecule of carbon dioxide is removed, and calcium benzoate is formed. Sodium amalgam converts phthalic acid into di-, tetra-, and hexa-hydrophthalic acids.

*Esters.* The behavior of phthalyl chloride (see below) seems to indicate that this compound has a lactone structure, with both chlorine atoms attached to the same carbon atom, and hence it was expected that two series of esters would exist. This, however, is not the case. The same esters are formed from silver phthalate and alkyl iodides, as from phthalyl chloride and alcohols (*Graebe*, Ber. 16, 860). Dimethyl phthalate, b.p.  $280^\circ$ ; diethyl phthalate, b.p.  $288^\circ$  (*Graebe*, Ann. 238, 318). The diethyl ester is sometimes used, on account of its bitter taste, for denaturising alcohol. These esters condense with ethyl acetate, acetone or similar compounds, in the presence of sodium ethoxide to form *diketo-hydrindene derivatives* (p. 599). Diphenyl phthalate, m.p.  $70^\circ$  (*Schroeder*, Ber. 7, 703; *Pawlewski*, Ber. 28, 108).

Hydrogen phthalic esters,  $C_6H_4 \begin{matrix} \swarrow COOH \\ \searrow COOR \end{matrix}$ , are formed when an alcohol, ROH, is

heated with phthalic anhydride. Methyl hydrogen phthalate, m.p.  $84^\circ$ ; ethyl hydrogen phthalate, m.p.  $47-48^\circ$ . Most hydrogen phthalic esters crystallise well, and form crystalline salts with organic bases. They are useful for resolving alcohols with an asymmetric carbon atom. The hydrogen phthalate of the alcohol in question is prepared, and this is combined with an optically active base, and the alcohol is recovered from the salt formed. Many hydrogen phthalates have been prepared for this purpose, and others for the characterisation of alcohols.

**HALIDES.** Phthalyl fluoride,  $C_6H_4(COF)_2$ , *sym*-form, m.p.  $42-43^\circ$ , b.p.  $135^\circ$  (54 mm.), has been prepared by *Dann* and co-workers (J., 1933, 16) from the *sym*-chloride and sodium fluoride at  $250-300^\circ$ , or zinc fluoride at  $60^\circ$ . The

chloride of the acid ethyl ester, obtained from ethyl hydrogen phthalate by the action of phosphorus trichloride, is an unstable oil (Ber. 20, 2011).

Phthalyl chloride,  $\text{C}_6\text{H}_4 \begin{matrix} \text{[1]COCl} \\ \text{[2]COCl} \end{matrix}$  and  $\text{C}_6\text{H}_4 \begin{matrix} \text{[1]CO} \\ \text{[2]CCl}_2 \end{matrix} \text{O}$ . The symmetrical chloride, m.p. 15–16°, is formed by the action of phosphorus pentachloride on the acid in an open vessel, and at a temperature not exceeding 150°. When it is heated with aluminium chloride for some time on a water bath, it is converted into the asymmetrical chloride, m.p. 89° (Ott, Org. Synth. 10, 94). The asymmetrical chloride boils at 276°, reverting to the symmetrical form. The latter readily reacts with alcohols and bases, and can be reduced to *o*-phthalyl alcohol with acetic acid and sodium amalgam. The asymmetrical lactonic form is much less reactive (Ott, Ann. 392, 245). Both forms react in the same way with sodio-acetoacetic ester (Scheiber, Ber. 46, 2366). The equilibrium between the two forms has been investigated by Csanyi (Mo. 40, 31). The asymmetric structure explains the reaction of phthalyl chloride and zinc and acetic acid, when it is converted into phthalide (p. 376), diphtalyl,  $\text{C}_6\text{H}_4 \begin{matrix} \text{CO} & \text{CO} \\ \diagdown & / \\ \text{O} & \text{O} \\ \diagup & \diagdown \\ \text{C} & \text{C} \end{matrix} \text{C}_6\text{H}_4$ , and hydro-

diphtalyl and its reaction with benzene and aluminium chloride, when it gives phthalophenone (diphenyl-phthalide) (cf. sulpho-benzoyl-dichloride). In this reaction, the symmetrical chloride also gives anthraquinone and *o*-benzoyl-benzoic acid, and the asymmetrical form gives *ms*-diphenyl-anthrone (p. 653) (Copisarov, J. 111, 10). Lead thiophanate reacts with phthalyl chloride to form di-(thiophenyl)-phthalide,  $\text{C}_6\text{H}_4 \begin{matrix} \text{C(SC}_6\text{H}_5)_2 \\ \text{CO} \end{matrix} \text{O}$ , m.p. 85°, which is oxidised by permanganate to di-(phenyl-sulphone)-phthalide, m.p. 194°, a compound also obtained directly from phthalyl chloride and sodium benzene-sulphinate (Troeger, J. pr. 66, 345).

*o*-Phthalylene tetrachlorides: By the action of phosphorus pentachloride on phthalyl chloride, two isomeric phthalylene tetrachlorides are formed, one with an indefinite m.p. 85–86°, and the other melting sharply at 43°. The one with

the higher m.p. is the lactone chloride,  $\text{C}_6\text{H}_4 \begin{matrix} \text{CCl}_2 \\ \diagdown & / \\ & \text{O} \\ \diagup & \diagdown \\ \text{CCl}_2 \end{matrix}$ , and the other the acid

chloride,  $\text{C}_6\text{H}_4 \begin{matrix} \text{CCl}_2 \\ \diagdown & / \\ & \text{COCl} \end{matrix}$ ; this follows from the different rates of reaction of the

compounds with aniline, and other reasons (Ott, Ber. 55, 2108). When the *sym*-form is distilled at ordinary pressure (b.p. 90–105° [0.2 mm.]) it is partly converted into the *as*-form (b.p. 115–120° [0.2 mm.]). The latter is also obtained by the action of phosphorus pentachloride on phthalide chloride (Claus, Ber. 19, 1188). It condenses with benzene in presence of aluminium chloride or concentrated sulphuric acid to give diphenyl-anthrone (p. 653) (Haller, C.r. 121, 102).

Phthalic anhydride,  $\text{C}_6\text{H}_4 \begin{matrix} \text{[1]CO} \\ \text{[2]CO} \end{matrix} \text{O}$ , m.p. 128°, b.p. 248°, sublimes readily in long needles. It is obtained by melting phthalic acid, or heating the latter with acetyl chloride (Anschütz, Ber. 10, 326); by the catalytic oxidation of naphthalene vapour with oxygen or air in the presence of vanadium pentoxide, vanadium oxychloride, or molybdenum oxides; and by the action of concentrated sulphuric acid on  $\alpha$ -nitro-naphthalene, followed by fusion with iron or zinc turnings (Br. Pats. 145,701 and 153,252). Phthalic anhydride forms condensation products as readily as benzaldehyde (p. 268); with acetic acid, phthalyl-acetic acid is formed; with malonic or acetoacetic ester, alkylidene-phthalides are obtained, or at a higher temperature, fatty acids are formed, with elimination of carbon dioxide. In the presence of aluminium chloride it condenses with bromobenzene to *p*'-bromo-*o*-benzoyl-benzoic acid, m.p. 173°, which, under the influence of sulphuric acid, undergoes ring closure, with formation of 2-bromo-anthraquinone (p. 657). With diphenyl it forms first *p*'-phenyl-*o*-benzoyl-benzoic acid and then 2-phenyl-anthraquinone. For its condensation with  $\alpha$ - and  $\beta$ -naphthol, see Rieche, Ber. 64, 1603. It condenses with phthalide to give diphtalyl, and with phenols to

give phthaleins, a group of triphenylmethane dyes, which includes some beautifully fluorescent compounds. **Phthalyl sulphide**,  $C_6H_4(CO)_2S$ , m.p. 113–114, and

**diphthalyl disulphide**,  $C_6H_4 \begin{array}{c} \diagup CO \cdot S \cdot CO \diagdown \\ \diagdown CO \cdot S \cdot CO \diagup \end{array} C_6H_4$ , m.p. 330–332°, are obtained by

the action of hydrogen sulphide on *o*-phthalyl chloride at elevated temperatures; **phthalyl selenide**,  $C_6H_4(CO)_2Se$ , yellow crystals, m.p. 126–127°, is obtained by the action of hydrogen selenide on *o*-phthalyl chloride in the presence of aluminium chloride (*Reissert*, Ber. 44, 3027; *Szperl*, Roczn. Ch. 10, 654; 12, 378).

**Monoperphthalic acid**,  $C_6H_4(COOH)COOOH$ , m.p. 110° (decomp.), and **phthalic acid peroxide**,  $(COOH \cdot C_6H_4 \cdot CO)_2O_2$ , m.p. 156° (decomp.), are formed when phthalic anhydride is shaken with alkaline hydrogen peroxide. The former is readily soluble in water, but the latter only sparingly. **Diethyl-peroxido-phthalate**, m.p. 59°, is obtained by the action of alkaline hydrogen peroxide on the chloride of ethyl hydrogen phthalate. **Phthalyl peroxide**,  $C_6H_4(CO_2)_2$ , m.p. 133° (decomp.), deflagrates when rapidly heated, and is obtained by the action of sodium peroxide on phthalyl chloride. It is insoluble in all solvents. It gives monoperphthalic acid with one mol. of cold aqueous sodium hydroxide (*Baeyer*, Ber. 34, 762).

**Phthalamic acid**,  $C_6H_4 \begin{array}{c} \diagup [1]COOH \\ \diagdown [2]CONH_2 \end{array}$  or  $C_6H_4 \begin{array}{c} \diagup [1]C(NH_2)OH \\ \diagdown [2]CO \end{array} O$ , m.p. 148°, is formed by the action of ammonia on phthalic anhydride, and by the action of baryta water on phthalimide (*Aschen*, Ber. 19, 1399). **Anilic acid**, m.p. 192°.

**Phthalic diamide**,  $C_6H_4 \begin{array}{c} \diagup [1]CONH_2 \\ \diagdown [2]CONH_2 \end{array}$  or  $C_6H_4 \begin{array}{c} \diagup [1]C(NH_2)_2 \\ \diagdown [2]CO \end{array} O$ , m.p. 140–160°, with formation of phthalimide. It is also produced by the action of ammonia on ethyl phthalate or phthalyl chloride (*Auger*, Bull. 49, 345; Ann. ch. ph. 6, 22, 289; *Hoogewerff*, Rec. 11, 88; *Dunlap*, Am. 25, 612).

**Phthalimide**,  $C_6H_4 \begin{array}{c} \diagup [1]CO \\ \diagdown [2]CO \end{array} NH$  or  $C_6H_4 \begin{array}{c} \diagup [1]C(=NH) \\ \diagdown [2]CO \end{array} O$  (phthal-iso-imide), m.p. 238°, is prepared by the action of gaseous or aqueous ammonia at 300° on phthalyl chloride or phthalic anhydride (*Noyes*, Org. Synth. 11, 522). It is formed when phthalic acid is heated with ammonium thiocyanate (*Liebermann*, Ber. 19, 2283) or with urea (*Herzog*, Angew. 32, 301), from phthalamide, and from *o*-cyano-benzoic acid (p. 387) by intramolecular rearrangement (*Scheiber*, Ber. 46, 2366). With alcoholic potash it forms **potassio-phthalimide**,  $C_6H_4(CO)_2NK$ , from which heavy-metal salts can be obtained by double decomposition. By acting upon it with alkyl and aryl halides, a large number of amines can be made. It is not necessary to isolate potassio-phthalimide in this reaction, as alkyl-phthalimides are formed on simply heating a mixture of phthalimide, alkyl halide, and potassium carbonate (*Ing*, J. 1926, 2348). The alkyl-imides thus formed have a symmetrical structure,  $C_6H_4(CO)_2NR$ , e.g., **sym-methyl-** and **sym-benzyl-phthalimides**, m.p. 132 and 115°, resp. Phthalalkylamic

acids, and acetyl chloride, however, form *as*-alkyl-imides,  $C_6H_4 \begin{array}{c} \diagup C:(NR) \\ \diagdown CO \end{array} O$ :

**as-methyl-phthalimide**, m.p. 78°, **as-benzyl-phthalimide**, m.p. 81° (*Hoogewerff*, Rec. 13, 93). **Allyl-phthalimide**, m.p. 71°; **propenyl-phthalimide**, m.p. 151° (*Johnson*, Am. J. 45, 343).

**Bromomethyl-phthalimide**,  $C_6H_4(CO)_2NCH_2Br$ , m.p. 150°, is the bromination product of *sym*-methyl-phthalimide, and with water gives **hydroxymethyl-phthalimide**,  $C_6H_4(CO)_2N \cdot CH_2OH$ , which is also obtained by the combination of phthalimide with formaldehyde at 100°, and easily decomposes into these substances. It condenses with benzene hydrocarbons under the influence of concentrated sulphuric acid, to give benzyl-phthalimides (Ger. Pat. 134,980). Ethyl-phthalimide and alkyl-magnesium halides give products of the type

$C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown C(OH)Alk \end{array} NC_2H_5$  (*Sachs*, Ber. 37, 385). **N-β-hydroxyethyl-phthalimide**,

$C_6H_4(CO)_2N \cdot CH_2CH_2OH$ , m.p. 88–89°, is prepared from potassio-phthalimide and ethylene chlorhydrin (*Dersin*, Ber. 54, 3158).

Phthalimide is reduced in acid solution to *phthalimidine* (p. 376), and in alkaline solution with zinc dust and caustic soda to *hydroxy-phthalimidine* (p. 381); with bromine and alkali, *anthranilic acid* is formed, presumably with the intermediate formation of *bromyl-phthalimide*,  $C_6H_4(CO)_2NBr$ , m.p. 206–207°. This latter can also be prepared by treating sodio-phthalimide in water with one mol. of bromine at 0°. *Chloryl-phthalimide*,  $C_6H_4(CO)_2NCl$ , m.p. 183–185°, is produced by the action of chlorine on phthalimide suspended in water (Ger. Pat. 139,553). These compounds react with sodium alkylates to form *carboxalkyl-anthranilic esters* as primary products (*Bredt*, Ber. 33, 21).

*sym*-Phthalanil,  $C_6H_4(CO)_2N \cdot C_6H_5$ , m.p. 208°, is obtained by the action of aniline on phthalic acid, and *as*-phthalanil,  $C_6H_4 \begin{array}{c} \diagup C(NC_6H_5) \diagdown \\ \diagdown CO \diagup \end{array} O$ , yellow, m.p.

125–126°, is obtained by the action of acetyl chloride on phthalanilic acid (*Graebe*, Ber. 32, 1991; *Prutti*, Ber. 36, 996; *Dunlap*, Am. 25, 612), together with a colourless isomer, m.p. 83–84°, of unknown constitution (*Kuhara*, Mem. Kyoto, 2, 365). When agitated with a concentrated solution of potassium carbonate it changes into the symmetrical anil (*Pummerer*, Ber. 45, 292). For substituted phthalanils, see *Kuhara, loc. cit.* *Phthalyl-diphenyl hydrazide*,  $C_6H_4(CONH \cdot NHC_6H_5)_2$ , m.p. 161°. *Phthalyl-hydrazine*,  $C_6H_4(CONH)_2$ , subliming at 200°, is obtained from phthalic anhydride and hydrazine hydrate; an isomeric product is obtained by the action of hydrazine on phthalimide (*Foersterling*, J. pr. 51 371; *Curtius*, J. pr. 54, 66).  $\alpha$ -Phthalyl-phenylhydrazine,  $C_6H_4(CO)_2N \cdot NH \cdot$

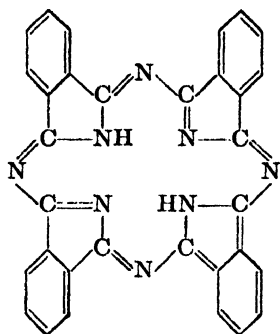
$C_6H_5$ , m.p. 178°.  $\beta$ -Phthalyl-phenylhydrazine,  $C_6H_4 \begin{array}{c} \diagup CONH \diagdown \\ \diagdown CONC_6H_5 \diagup \end{array}$ , m.p. 210°

(*Pickett*, Ann. 232, 225; *Huthe*, J. pr. 35, 265). *Phthalyl-hydroxylamic acid*,  $C_6H_4(COOH)C(OH)NOH$ , m.p. 220° (decomp.), obtained from phthalic anhydride and hydroxylamine in the cold, is converted into *phthalyl-hydroxylamine*,  $C_6H_4(CO)_2NOH$ , m.p. 230°, when the solution is heated, and both are converted into anthranilic acid by alkali (Ger. Pats. 130,302, 135,836, 136,788). *Phthalic diazide*,  $C_6H_4(CO \cdot N_3)_2$ , m.p. 56° (decomp.), an explosive substance, is prepared by the action of sodium azide on *sym*-phthalyl chloride in acetone solution (*Lindemann*, Ann. 464, 237). *Ethylene-diphthalimide*,  $(C_6H_4[CO]_2N \cdot CH_2)_2$ , m.p. 232°, obtained by the action of ethylene bromide on potassio-phthalimide, gives ethylene-diamine (Vol. I, p. 384) when boiled with aqueous potash (*Putochin*, C. 1928, I, 318).

*Phthalyl-glycocoll*,  $C_6H_4(CO)_2NCH_2COOH$ , m.p. 192°, is prepared by adding glycocoll slowly to fused phthalic anhydride. Its ester undergoes rearrangement under the influence of sodium ethoxide, giving *hydroxy-isocarboxystyric ester* (*Gabriel*, Ber. 33, 981; *Jurgens*, Ber. 40, 4409). Its chloride, m.p. 85°, decomposes on distillation at ordinary pressures, into carbon monoxide and chloromethyl-phthalimide,  $C_6H_4(CO)_2N \cdot CH_2Cl$ . *Phthalyl-alanine*,  $C_6H_4(CO)_2N \cdot CH(CH_3)COOH$ , m.p. 162°; chloride, m.p. 73°;  $\beta$ -phthalimido-propionic acid,  $C_6H_4(CO)_2N \cdot CH_2 \cdot CH_2COOH$ , m.p. 151°; chloride, m.p. 108° (*Gabriel*, Ber. 38, 633; 41, 242).

**PHTHALIC NITRILES.** *o*-Cyano-benzoic acid, m.p. 184°, is prepared by the action of nitrous acid and cuprous cyanide on anthranilic acid, and by the action of ammonia on benzoyl fluoride (*Dann*, J. 1933, 15). It undergoes rearrangement into the isomeric phthalimide when heated (*Sandmeyer*, Ber. 18, 1496; *Liebermann*, Ber. 19, 2283; *Hoogewerff*, Rec. 11, 84). For other methods of formation, see *Scheiber*, Ber. 45, 2398. *Methyl-o-cyano-benzoate*, m.p. 50–51° (*Rupe*, Helv. 13, 457); *ethyl ester*, m.p. 70° (*Muller*, Ber. 19, 1491). *o*-Cyano-benzotrichloride,  $CN[2]C_6H_4CCl_3$ , m.p. 94°, b.p. 280°, is obtained from *o*-tolunitrile (*Gabriel*, Ber. 20, 3197). *o*-Cyano-benzamide, m.p. 173°, is formed, together with other products, when phthalimide is heated with acetic anhydride for a short time, and by the action of hydroxylamine on *o*-cyano-benzal chloride (p. 381). When heated beyond its m.p., it isomerises to imido-phthalimide, and on boiling with an excess of acetic anhydride, it gives *o*-phthalonitrile,  $C_6H_4[1,2-(CN)]_2$ , m.p. 141°, which is also obtained from *o*-amino-benzonitrile through the diazo-compound (*Braun*, Ber. 40, 2709).

When *o*-cyano-benzamide and *o*-phthalonitrile are heated with metals, metallic compounds of dyes of the phthalocyanine class are formed (*Linstead, J. 1934, 1016*). The following formula



which resembles that of porphyrin, has been proposed for the parent substance. The imido-hydrogen atoms can be replaced by metals.

**SUBSTITUTED *o*-PHTHALIC ACIDS.** These compounds are obtained either by direct substitution, or by the oxidation of substituted naphthalenes and toluic acids. Halogeno-phthalic acids can also be prepared by Sandmeyer's method from the diazotised esters, but not from the acids themselves (*Blicke, Am. 51, 1865*). The mono- and di-chlorophthalic acids are all known.

4-Chlorophthalic anhydride, m.p. 98°, b.p. 297°.

3-Chlorophthalic anhydride, m.p. 126°, b.p. 313°.

4,5-Dichlorophthalic anhydride, m.p. 186°, b.p. 313°.

3,4-Dichlorophthalic anhydride, m.p. 121°, b.p. 329° } *Villiger, Ber. 42, 3532.*

3,6-Dichlorophthalic anhydride, m.p. 191° b.p. 339° }

3,5-Dichlorophthalic anhydride, m.p. 89° (*Crossley, J. 81, 1533*).

3,4,6-Trichlorophthalic anhydride, m.p. 148° } (*Gräbe, Ann. 149, 18; Ber.*

Tetrachlorophthalic anhydride, m.p. 250° } *34, 2107*).

The mono-, tri-, and tetrachloro-phthalic acids are obtained from the corresponding chloro-*o*-toluic acids, and chloro-naphthalene by oxidation. 4,5-, 3,4-, and 3,6-Dichlorophthalic acids are formed together when chlorine is passed into a solution of phthalic anhydride in fuming sulphuric acid, and the 3,5-acid is formed in small yield by the action of phosphorus pentachloride on dimethyl-dihydroresorcinol (Vol. II, p. 112).

**Tetrachloro-phthalyl chloride**, m.p. 137° (*as-form*), obtained by heating the anhydride with phosphorus pentachloride in a sealed tube at 220°, changes into the symmetrical form m.p. 48°, when heated. The asymmetrical form is slowly re-formed especially in the presence of animal charcoal (*Kirpal, Ber. 62, 2102*). **Tetrachloro-phthalimide**, m.p. 339°; **tetrachloro-phthalanil**, m.p. 274-275° (*Pratt, Am. 40, 98*).

**3-Bromophthalic acid**, m.p. 177-178°, anhydride, m.p. 130-131°, is prepared by reducing 3-nitrophthalic acid, diazotising, and boiling with cuprous bromide (*Stephens, Am. 43, 1950*).

**4,5-Dibromophthalic acid**, m.p. 135°, anhydride, m.p. 214°, obtained by brominating phthalic anhydride dissolved in concentrated sulphuric acid, or by oxidising dibromo-naphthalene with nitric acid, gives 4,5-dihydroxy-phthalic acid when boiled with potash (*Brück, Ber. 34, 2741; Seuerin, C. 1907, I, 1119*).

**3- and 4-IODOPHTHALIC ACIDS**, m.p. 206° and 182°, respectively (*Willgerodt, Ber. 29, 1575*). **3,4-Di-iodophthalic acid**, m.p. 212-213°, anhydride m.p. 198.5°. **3,6-Di-iodophthalic acid** is converted into its anhydride, m.p. 235°, when heated; **4,5-di-iodophthalic acid**, m.p. 221-222° (*Edinger, J. pr. 53, 375*). **Tetra-iodophthalic acid**, m.p. 324-327° (*Rupp, Ber. 27, 1634; Pratt, Am. 40, 198*).

**3- and 4-NITROPHTHALIC ACIDS**, m.p. 219° and 161°, respectively, are formed together in the nitration of phthalic acid; their anhydrides melt at 164°

and 114°, respectively; imides, m.p. 216° and 202°, respectively. The 3-nitrophthalimide is used as a reagent for the detection of organic halogen compounds (*Sah*, Ber. 65, 1630). 3-Nitrophthalyl chloride, m.p. 77° (*Anwerk*, Ber. 34, 3735; *Seidel*, Ber. 34, 4351; *Chambers*, Am. 25, 601; *Miller*, Indian J. 7, 619). For the formation of methyl hydrogen 3-nitro-phthalates,  $\alpha$ - m.p. 144°, and  $\beta$ - m.p. 157°, and their relation to V. Meyer's esterification rule (p. 296), see *Kahn*, Ber. 35, 3857.

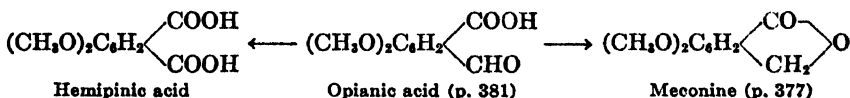
4-Azoxy-phthalic acid, forms salmon-coloured crystals with a double m.p., 228° and 300°. It is obtained by heating 4-nitrophthalic acid with alcoholic potash. 4-Azophthalic acid, m.p. above 340°, is produced when the nitro-acid is reduced with sodium amalgam; methyl ester, m.p. 124–126° (*Sachs*, Mo. 37, 53, 57). More vigorous reduction of the nitrophthalic acids produces 3- and 4-amino-phthalic acids (*Kauffmann*, Ber. 36, 2491). 4-Nitrophthalic acid crystallises with 1 H<sub>2</sub>O, m.p. 162° (anhydrous); it is obtained from 5-nitro-*o*-toluinitrile by oxidation with permanganate (*Mayer*, J. pr. 92, 137).

Sulphophthalic acid is obtained by heating naphthols, naphthylamines, or naphthalene-sulphonic acids with concentrated sulphuric acid and mercury at 220–300° (*Græbe*, Ber. 29, 2806). The action of sulphur trioxide on phthalic anhydride gives 4-sulphophthalic anhydride, a solid resin, and, if mercuric salts are present, 3,5-disulphophthalic anhydride, a resinous substance. In both these acids, the sulpho group can be replaced by chlorine by treatment with thionyl chloride or hydrochloric acid and sodium chlorate, and 4-chlorophthalic acid, b.p. 294°, and 3,5-dichlorophthalic acid, m.p. 164°, are formed (*Waldmann*, Ann. 487, 287). For the directing effect of mercuric sulphate in the sulphonation of phthalic anhydride, see *Lauer*, J. pr. 138, 87.

**HYDROXY-*o*-PHTHALIC ACIDS.** These acids are characterised by the melting points of their anhydrides, into which they are readily converted by heating.

3-Hydroxy-*o*-phthalic anhydride, m.p. 198–199°. 3-Methoxy-phthalic acid, m.p. 173–174°; anhydride, m.p. 160° (*Corbellini*, Gazz. 61, 281). Dinitro-3-hydroxy-*o*-phthalic acid, also called *juglonic acid*, is formed by the action of nitric acid on juglone, a naphthalene derivative (Vol. II, p. 426). 4-Hydroxy-*o*-phthalic anhydride, m.p. 171° (*Bentley*, J. 91, 98). *p*-Dihydroxy-*o*-phthalonitrile, *o*-dicyano-hydroquinone, (HO)<sub>2</sub>[3,6]C<sub>6</sub>H<sub>2</sub>[1,2](CN)<sub>2</sub> + 2H<sub>2</sub>O, is obtained by the action of nascent hydrogen cyanide on quinone. When acted upon by hot concentrated sulphuric acid it is converted into dihydroxy-phthalimide, C<sub>6</sub>H<sub>2</sub>(OH)<sub>2</sub>(CO)<sub>2</sub>NH, which, on boiling with hydrochloric acid loses carbon dioxide, and gives *p*-dihydroxy-benzoic acid (*Thiele*, Ber. 33, 675; Ann. 349, 45). 3-Hydroxy-5-methyl-*o*-phthalic acid,  $\beta$ -coccinic acid, m.p. 163–164°, is obtained by heating cochineal; its methyl ether has been prepared from 3-methoxy-*o*-toluic ester by condensation with chloral and oxidation of the resulting trichlorophthalide-carboxylic acid. The methyl ether of the isomeric 3-methyl-5-hydroxy-phthalic acid,  $\gamma$ -coccinic acid, is also formed in this reaction (*Meldrum*, J. 99, 1712). 4-Methoxy-phthalic acid, m.p. 144°, is obtained by the action of permanganate on 2,6-dimethoxy-naphthalene (*Chakravarti*, Indian J. 10, 693).

Norhemipinic acid, 3,4-dihydroxy-phthalic anhydride, m.p. 238°, is prepared by heating the reaction product of hemipinic acid and phosphorus pentachloride at 180°, 3,4-dichloro-methoxy-phthalic anhydride, (ClCH<sub>2</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CO)<sub>2</sub>O, m.p. 155°, with water. Hemipinic anhydride, 3,4-dimethoxy-phthalic anhydride, m.p. 167°. Free hemipinic acid, m.p. 187°, has been obtained by oxidising opianic acid with lead dioxide and sulphuric acid (*Edwards*, J. 127, 195), (together with opianic acid and meconine) by oxidising narcotine, and (together with meconine) by fusing opianic acid with potash (*Arch. pharm.* 271, 288).



For hemipinic ester-acids, hemipinamic acids, and hemipininimides etc., see *Hoogewerff*, Rec. 14, 252; *Wegscheider*, Mo. 18, 589; 24, 375; *Kirpal*, Ber. 35, 677.

6-Amino-hemipinic acid is obtained from the so-called azo-opianic acid, 2,3-dimethoxy-5,6-anthranil-carboxylic acid (p. 382), by boiling with baryta water.

**Nor-meta-hemipinic anhydride**, 4,5-dihydroxy-phthalic anhydride, m.p. 247°. **Meta-hemipinic anhydride**, m.p. 179°. **Meta-hemipinic acid**, 4,5-dimethoxy-*o*-phthalic acid, m.p. 202-204°, a degradation product of papaverine, has been synthesised by *Fargher and Perkin* (J. 119, 1724) by oxidising 4,5-dimethoxy-tolyl-methyl-ketone with permanganate. **Hydrastic acid**,  $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_2(\text{COOH})_2$ , is an oxidation product of hydrastinine anhydride, m.p. 179°. Meta-hemipinic and hydrastic acids have also been found among the degradation products of podophyllotoxine (Vol. II, p. 492). When cotarnine is oxidised it gives **cotarnic acid**, or **methylene-methyl-ether-3,4,5-trihydroxy-*o*-phthalic acid**,  $(\text{CH}_2\text{O})_2(\text{CH}_3\text{O})-\text{C}_6\text{H}(\text{COOH})_2$ . **3,4,5-Trimethoxy-*o*-phthalic acid**, m.p. 174°, anhydride m.p. 143°, is prepared from trimethyl-gallic acid by condensation with chloral hydrate, hydrolysis to the phthalide-carboxylic acid, transformation into phthalide, and oxidation (*Bargellini*, *Lincei* 21, II, 146).

**Isophthalic acid**, benzene-*m*-dicarboxylic acid,  $\text{C}_6\text{H}_4$   $\begin{matrix} \swarrow [1]\text{COOH} \\ \searrow [3]\text{COOH} \end{matrix}$ ,

m.p. 325° (sublimes) (*Aschan*, *Ber.* 60, 1927), is formed in the oxidation of *m*-xylene or *m*-toluic acid with chromic acid or permanganate (*Ullmann*, *Ber.* 36, 1798); from *m*-xylene bromide (p. 372) by the action of alcoholic potash and oxidation of the resulting *m*-phthalylethyl ether (*Kipping*, *Ber.* 21, 47); and from *m*-dicyano-benzene and *m*-cyano-benzoic acid (see below). The last two methods are steps in the nuclear syntheses from the corresponding amino-compounds, *m*-phenylene diamine, and *m*-amino-benzoic acid. Potassium benzoate, *m*-bromo-benzoate, and *m*-sulpho-benzoate give isophthalic acid when fused with sodium formate, terephthalic acid being a by-product in the first two cases. It is also produced by the action of sodium amalgam and ethyl chlorocarbonate on *m*-dibromo-benzene, by heating hydro-pyromellitic and hydro-prehnitic acids (p. 396), on fusing humic acid, obtained from coal, with potash (*Tropsch*, *C.* 1924, I, 600), and by the action of nitric acid on pinabietic acid (*Aschan*, *Ber.* 60, 1923).

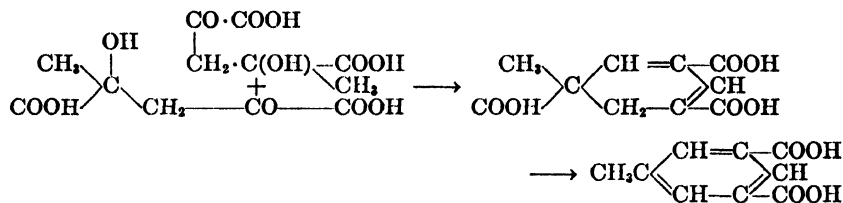
Isophthalic acid is soluble in 460 parts of boiling and 7800 parts of cold water. It does not form an anhydride. On reduction it gives tetrahydro-isophthalic acid. Its barium salt,  $\text{C}_6\text{H}_4(\text{CO}_2)_2\text{Ba} + 6\text{H}_2\text{O}$ , is readily soluble in water, unlike those of phthalic and terephthalic acids (*Ann.* 260, 30). Dimethyl ester, m.p. 64°; dichloride, m.p. 41°, b.p. 276° (*Auwers*, *Ber.* 46, 457). Its dihydrazide, m.p. 220°, gives, with nitrous acid, isophthalazide,  $\text{C}_6\text{H}_4(\text{CON}_2)_2$ , m.p. 56°, and when this is boiled with ethyl alcohol, *m*-phenylene-urethane,  $\text{C}_6\text{H}_4(\text{NHCO}_2\text{C}_2\text{H}_5)_2$ , is formed (*Curtius*, *J.* pr. 54, 66).

***m*-Cyano-benzoic acid**, m.p. 223°, ethyl ester, m.p. 56° (*Rupe*, *Helv.* 13, 457). For the action of hydrazine on this acid, see *Curtius*, *J.* pr. 125, 40. ***m*-Dicyano-benzene**, m.p. 162° (*Bogert*, *Am.* 26, 464).

**SUBSTITUTED ISOPHTHALIC ACIDS.** 5-Chloro-, 5-iodo-, and 5-amino-isophthalic acids are prepared from 5-nitro-isophthalic acid, itself obtained by the nitration of isophthalic acid. Sulphonation gives 5-sulpho-isophthalic acid, cf. benzoic acid (pp. 315, 332). 4-Bromo-, 4-iodo-, 4-amino- and 4-sulpho-isophthalic acids are prepared by oxidising the corresponding toluic acids (*Coule*, *Ber.* 14, 2278; *Schiff*, *Ber.* 24, 3778; *Lowenherz*, *Ber.* 25, 2795; *Meyer*, *Ber.* 28, 34). 2-Nitro- and 2-amino-isophthalic acids are obtained from 2-nitro-*m*-xylene (*Noelting*, *Ber.* 39, 73). 4-Chloro-isophthalic acid, m.p. 294°, 4-acetamino-isophthalic acid, m.p. 289°, and 4,6-diamino-isophthalic acid are obtained from chloro-, acetamino-, and diacetamino-*m*-xylenes by oxidation with permanganate (*Ullmann*, *Ber.* 36, 1799, 1803; *Bogert*, *Am.* 31, 841). Tetrachloro-, tetrabromo-, and tetraiodo-isophthalic acids, m.p. 181°, 290°, and 310° respectively (*Rupp*, *Ber.* 29, 1632). Tetra-amino-isophthalic acid,  $\text{C}_6(\text{NH}_2)_4(\text{COOH})_2$ , has been ob-

tained starting with isopurpuric acid, which appears to be the dinitrile of a dinitro-hydroxylamino-hydroxy-isophthalic acid (p. 201).

**HOMOLOGUES OF ISOPHTHALIC ACID.** Three methyl-isophthalic acids are possible. The most interesting is **uvitic acid**, *5-methyl-isophthalic acid*,  $\text{CH}_3[\text{5}]\text{C}_6\text{H}_3[1,3](\text{COOH})_2$ , m.p.  $287^\circ$ , which is obtained by oxidising mesitylene with dilute nitric acid, or, synthetically, from pyruvic acid (p. 26). The latter synthesis is carried out as follows. When pyruvic acid is boiled with baryta water, or better, sodium hydroxide solution, a condensation product of aldol type, *p-pyruvic acid*, is formed. Two molecules of the latter condense to form *methyl-dihydro-trimesic acid*, water and oxalic acid being eliminated. On prolonged boiling with baryta water, or better by the action of concentrated sulphuric acid, carbon dioxide and two hydrogen atoms are eliminated, and uvitic acid is formed (Wolff, Ann. 305, 125):



When a mixture of pyruvic acid and propyl aldehyde or isobutyl-aldehyde is used, *5-ethyl-isophthalic acid* or *5-isopropyl-isophthalic acid*, respectively, is formed (Döbner, Ber. 23, 2377; 24, 1746). These acids are oxidised by chromic acid to trimesic acid (p. 395). When heated with lime, uvitic acid gives first *m*-toluic acid, and then toluene.

**Xylic acid**, *4-methyl-isophthalic acid*,  $\text{CH}_3[4]\text{C}_6\text{H}_3[1,3](\text{COOH})_2$ , m.p.  $282^\circ$ , is obtained by the action of dilute nitric acid on pseudo-cumene or *p*-xylic and isoxylic acids. It gives tri-mellitic acid when oxidised with permanganate (p. 396). **2-Methyl-isophthalic acid**, m.p.  $235^\circ$ , is obtained by the reduction of 2,6-dicarboxy-phenyl-glyoxylic acid with hydrogen iodide and phosphorus (Graebe, Ann. 290, 206).

**HYDROXY-ISOPHTHALIC ACIDS.** The same methods which serve for the preparation of hydroxy-benzoic acids from phenols, and of aldehydo-hydroxy-benzoic acids from phenolic aldehydes, may be used to convert them further into hydroxy-isophthalic acids. Amino- and sulpho-carboxylic acids can also be used as starting materials (Jacobsen, Ber. 16, 1966).

**2-Hydroxy, 4-hydroxy-, and 5-hydroxy-isophthalic acids**, m.p.  $243^\circ$ ,  $305^\circ$ , and  $288^\circ$ , respectively. **Ethyl 4-hydroxy-isophthalate**, m.p.  $57^\circ$ , is formed in small yield in a peculiar condensation which glutaconic ester undergoes in the presence of alcohol-free sodium ethylate (Pechmann, Ber. 37, 2117). The 5-acid is among the products of heating humic acid, from coal, under pressure (Tropsch, C. 1924, I, 601).

**5,2-Nitro-hydroxy-isophthalic acid**, m.p.  $214^\circ$ , is obtained from nitromalonic aldehyde and acetone-dicarboxylic acid (p. 25) (Hill, Am. Ch. J. 24, 1).

**4,6-Dihydroxy-isophthalic acid**, m.p.  $326^\circ$ , is obtained by heating resorcinol with potassium bicarbonate to  $180^\circ$  in a sealed tube (Hemmelmayer, Mo. 38, 84), and from 4,6-dibromo-*m*-xylene, which is oxidised step by step to 4,6-dibromo-isophthalic acid, m.p.  $250-254^\circ$ ; this is then boiled with sodium and copper acetates (Marzin, J. pr. 138, 108). **Dimethoxy-isophthalic acid**, m.p.  $272^\circ$  (decomp.) is obtained from 5-nitro-2,4-dimethoxy-benzoic ester, by replacing the  $\text{NO}_2$  group by  $\text{CN}$ , and hydrolysing the product (Späth, Ber. 64, 2210).

**Hydroxy-uvitic acids:** **4-Hydroxy-uvitic acid**,  $(\text{CH}_3)[5](\text{HO})[4]\text{C}_6\text{H}_3[1,3](\text{COOH})_2$ , m.p.  $295^\circ$ , is of interest since it is formed by the action of chloroform, chloral, or ethyl trichloroacetate on sodio-acetoacetic ester (p. 26); methenyl-bis-acetoacetic ester is probably an intermediate product (Claisen, Ann. 297, 11). It has also been prepared by the action of carbon tetrachloride and alkali on *o*-cresotic acid (Ger. Pat. 258,887).

***m*-Hydroxy-uvitic acid**,  *$\alpha$ -coccinic acid*,  $(\text{CH}_3)[6](\text{HO})[4]\text{C}_6\text{H}_3[1,3](\text{COOH})_2$ , m.p.  $320-332^\circ$  (decomp.), has been prepared by condensing 4-homosaliclic



methyl ether with chloral, oxidising the product to the dicarboxylic acid, and demethylating (*Shah*, Indian J. 8, 261).

**Terephthalic acid**,  $C_6H_4[1,4](COOH)_2$ , sublimes without melting. Terephthalic acid is obtained from *p*-benzene derivatives, such as *p*-xylene, *p*-toluic acid, *p*-cyano-benzoic acid, *p*-dicyano-benzene, *p*-dibromo-benzene, etc., in the same way as isophthalic acid is obtained from the corresponding *m*-derivatives. Small amounts are formed by the action of magnesium and carbon dioxide on *p*-dibromo-benzene (*Houben*, Ber. 38, 3796). It is best prepared by oxidising *p*-xylylene dibromide (p. 372), or *p*-toluic acid with alkaline permanganate (*Baeyer*, Ann. 245, 139; *Freyc*, J. pr. 43, 126).

Terephthalic acid is almost insoluble in water, alcohol, and ether. It can be reduced to di-, tetra-, and hexa-hydroterephthalic acids. It does not form an anhydride. Its barium salt,  $C_8H_4O_4Ba + 4H_2O$ , is very slightly soluble. Methyl ester, m.p.  $140^\circ$ ; chloride, m.p.  $78^\circ$ ; b.p.  $259^\circ$ ; aminic acid, m.p.  $214^\circ$ ; dihydrazide, m.p. above  $300^\circ$ ; diazide,  $C_6H_4[1,4](CON_3)_2$ , m.p.  $110^\circ$  (*Curtius*, J. pr. 54, 66).

**Diperterephthalic acid**,  $C_6H_4[1,4](COOOH)_2$ , forming sparingly soluble, explosive, needles, has been prepared by *Baeyer* (Ber. 34, 766) by the action of alcoholic hydrogen peroxide on terephthalyl chloride. It is precipitated from its alkaline solution as a mono-sodium salt by the action of carbon dioxide. Its ethyl ester,  $C_8H_4(CO_2 \cdot OC_2H_5)_2$ , m.p.  $37^\circ$ , was obtained from terephthalyl chloride and barium ethyl peroxide,  $Ba(O \cdot OC_2H_5)_2$ .

*p*-Cyanobenzoic acid,  $CN[C_6H_4COOH]$ , m.p.  $219^\circ$ , is obtained from ethyl *p*-aminobenzoate, or by oxidising *p*-tolunitrile with potassium persulphate. Ethyl ester, m.p.  $54^\circ$ . *p*-Dicyano-benzene,  $C_6H_4[1,4](CN)_2$ , m.p.  $223^\circ$ .

**Mononitro-terephthalic acid**, m.p.  $259^\circ$ , is formed in the nitration of sulpho-terephthalic acid; 2,3-, 2,6-, and 2,5-dinitro-terephthalic acids are also known (*Hausermann*, Ber. 28, 81). 2,5-Diamino-terephthalic acid,  $(NH_2)_2[2,5]C_6H_2[1,4](COOH)_2$ , is infusible; its diethyl ester is formed when diimino-succino-succinic ester is oxidised with bromine. This acid forms many condensation products in the same way as anthranilic acid, the grouping of which it has two-fold (*Bogert*, Am. 29, 729). For dihalogeno-terephthalic acids, see Br. Pat. 663,791, and for tetrachloro-, tetrabromo-, and tetraiodo-terephthalic acids, see *Rupp*, Ber. 29, 1625; *Lutjens*, Ber. 29, 2833.

**ALKYL-TEREPHTHALIC ACIDS.** 4-Methyl-terephthalic acid,  $\alpha$ -xylydic acid, m.p.  $282^\circ$ , is an oxidation product of pseudocumene, and 2,5-dimethyl-terephthalic acid,  $\beta$ -cumidic acid, is an oxidation product of durene (Ber. 19, 2510).

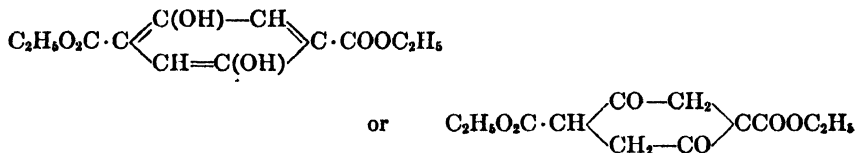
**HYDROXY-TEREPHTHALIC ACIDS.** Hydroxy-terephthalic acid, which sublimes without melting, is obtained from nitro-terephthalic acid. There are three possible dihydroxy-terephthalic acids, of which 2,5-dihydroxy-terephthalic acid should be mentioned on account of its relation to succino-succinic ester. Its diethyl ester is formed from the latter by removal of two hydrogen atoms by bromine or phosphorus pentachloride (*Levy*, Ber. 22, 2107). The same ester is formed by the action of sodium ethoxide on dibromo-acetoacetic ester (*Wedel*, Ann. 219, 78).

2,3-Dimethoxy-terephthalic acid,  $(CH_3O)_2[2,3]C_6H_2[1,4](COOH)_2$ , m.p.  $213$ – $214^\circ$ , is obtained by methylating and oxidising the product obtained by rearrangement of pyrocatechol diallyl-ether (p. 193) (*Kawai*, Res. Tokio 3, 263, 279).

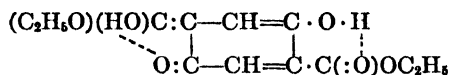
2,5-Dihydroxy-terephthalic acid,  $(HO)_2C_6H_2(COOH)_2$ , obtained from 2,5-dibromo-terephthalic acid by the action of sodium acetate (*Marzin*, J. pr. 138, 106), crystallises with  $2H_2O$  in a colourless form, and without water in a yellow form (*Hantzsch*, Ber. 48, 797). It gives a deep-blue colour with ferric chloride. When rapidly heated it breaks down into hydroquinone and two molecules of carbon dioxide. Diethyl 2,5-dihydroxy-terephthalate, m.p.  $133^\circ$ , also crystallises in two forms. At room temperature it forms stable, leaf-green prisms or plates, and at higher temperatures, or when sublimed, colourless leaflets. The reactions of this ester are chiefly those of a hydroxyl-derivative; thus, it does not

combine with hydroxylamine or phenylhydrazine, and it forms dialkyl ethers when acted upon by sodium and alkyl iodides. On the other hand, it does not react with phenyl isocyanate (p. 97), and shows certain analogies with succino-succinic ester (Vol. II, p. 146) (*Goldschmidt*, Ber. 23, 259). When reduced with zinc and alcoholic hydrochloric acid, it gives succino-succinic ester (*Baeyer*, Ber. 19, 432; *Noyes*, Ber. 22, 2169). With hydroxylamine hydrochloride it gives a dihydroxamic acid, and tetrahydro-dihydroxy-terephthalic acid is formed at the same time (*Jeanrenand*, Ber. 22, 1280).

*Hantzsch* (Ber. 22, 1294) regarded the two forms of ethyl dihydroxy-terephthalate, and of analogous compounds, as an example of tautomerism, ascribing a quinone formula to the coloured modification, and a hydroxyl-formula to the colourless one. *Nef* (Am. J. 12, 379) and *Goldschmidt* (Ber. 23, 260) do not regard colour as a reliable criterion for a keto-structure, and do not find the above tautomerism supported by chemical evidence.



Hantzsch later modified his view, and regarded the colourless forms as benzene derivatives, and the coloured ones as simple enol derivatives (Ber. 48, 797):



**Succino-succinic acid**, the ester of which gives ethyl 2,5-dihydroxy-terephthalate with elimination of two hydrogen atoms, is dealt with in Vol. II, p. 146, in connection with the hydroaromatic compounds.

3,5-Dihydroxy-terephthalic acid, m.p. 305°, is the direct carboxylation product of 3,5-dihydroxy-benzoic acid (*Brunner, Mo.* 50, 216).

**TRIHYDROXY-CARBOXYLIC ACIDS.** Phloroglucinol-dicarboxylic ester has been mentioned under the hydroaromatic compounds (Vol. II, p. 113) as a derivative of triketo-cyclohexane. Its formation by the condensation of three molecules of sodio-malonic ester is an example of benzene ring formation from aliphatic compounds. Gallo-carboxylic acid, trihydroxy-isophthalic acid, (HO)<sub>3</sub>[4,5,6]C<sub>6</sub>H[1,3](COOH)<sub>2</sub>, m.p. 283° (decomp.), is obtained, together with pyrogallol-carboxylic acid, when pyrogallol is heated at 130° with ammonium carbonate (Sennhofer, Ber. 13, 1876), or at 150–160° with sodium or potassium bicarbonate (Voswinckel, Ber. 45, 1242).

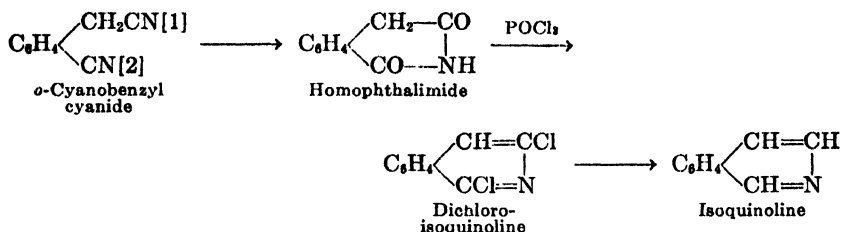
(b) **AROMATIC DICARBOXYLIC ACIDS** which contain one COOH in the nucleus and one COOH in the side-chain. The three  $\alpha$ -homophthalic or phenylacetic carboxylic acids are known. The *o*-acid readily gives rise to heterocyclic derivatives.

**Phenylacetic-*o*-carboxylic acid, *o*-*o*-homophthalic acid**,  $\text{COOH}[2]\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$ , m.p. 175°, with loss of water. It is obtained when gamboge is fused with KOH (Gabriel, Ber. 19, 1654). It can be obtained by the oxidation of indene (q.v.) or, better, *hydrindone* with potassium permanganate or chromic acid (Ingold, J. 123, 1469; Meyer, Ann. ch. ph. [10], 17, 271; Graebe, Ber. 31, 375), and by reduction of phthalonic acid with hydrogen iodide. It can also be obtained by hydrolysis of the corresponding nitrile. One of the two methylene hydrogen atoms in esters of the acid can be replaced by potassium, and then by the benzyl group, *benzyl-homophthalic acid*, m.p. 164°, being formed (Dieckmann, Ber. 47, 1428). It is oxidised by permanganate to *phthalide-carboxylic acid* (p. 439) (Stevens, J. 1928, 2827). Its anhydride melts at 141°, and in some reactions

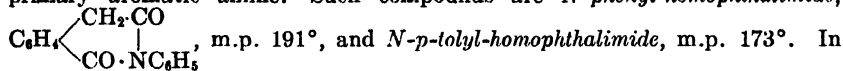
behaves as the enol form,  $C_6H_4 \begin{matrix} \text{CH:C-OH} \\ \text{CO-O} \end{matrix}$  (Davies, J. 1928, 1616). When heated, the anhydride loses CO, and becomes *hydrodiphthalo-lactonic acid* (Graebe,

Ber. 31, 376). 4-Nitrohomophthalic acid, m.p. 220° (decomp.) (*Ingold*, J. 123, 1469).

*o*-Homophthalimide, m.p. 233-234°, is obtained by heating the ammonium salt of the acid, and by the action of acids on the dinitrile. In the latter reaction, *o*-cyano-phenylacetic acid, which is the primary product, undergoes a rearrangement similar to that occurring when *o*-cyanobenzoic acid is converted into phthalimide (p. 387) (*Gabriel*, Ber. 23, 2478). When treated with POCl<sub>3</sub>, *o*-homophthalimide is converted into *dichloro-isoquinoline* which, on reduction with HI, gives *isoquinoline* (*Gabriel*, Ber. 27, 2492; *Damerov*, Ber. 27, 2232).



When heated with zinc dust, homophthalimide is directly converted into isoquinoline. When acted upon by caustic potash and alkyl halides, both hydrogen atoms of the methylene group are replaced by alkyl groups. This reaction does not work with homophthalic or phenylacetic esters. The mono-alkyl-*o*-cyanobenzyl cyanides give mono-alkyl-homophthalimides, which can be converted in the same manner as homophthalimide itself, into *alkyl-isoquinolines* (*Gabriel*, Ber. 20, 2499). Homophthalimide derivatives with aromatic residues attached to the nitrogen are formed when homophthalic acid is heated with a slight excess of a primary aromatic amine. Such compounds are *N*-phenyl-homophthalimide,



these bases, the CH<sub>2</sub> group retains its reactivity, a fact which is shown by the formation of benzylidene derivatives with benzaldehyde (*Meyer*, C.r. 193, 400). For azo-dyes prepared from homophthalimide, see *Meyer*, C.r. 192, 885; 193, 344.

*o*-Cyano-*o*-toluic acid, COOH[2]C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CN, m.p. 116° (decomp.). The potassium salt of this acid can be obtained by the action of potassium cyanide on phthalide (p. 376) (*Wislicenus*, Ann. 233, 102).

*o*-Cyanobenzyl cyanide, *o*-β-homophthalonitrile, CN[2]C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CN, m.p. 81°, is prepared from *o*-cyanobenzyl chloride (p. 376). When acted upon by caustic potash and an alkyl halide, one hydrogen atom of the methylene group can be replaced by an alkyl radical (see homophthalimide). With acetyl chloride it gives ψ-diacetyl-*o*-cyanobenzyl cyanide, CN·C<sub>6</sub>H<sub>4</sub>C(CN):C(CH<sub>3</sub>)OCOCH<sub>3</sub>, which can be converted into 3-methyl-isoquinoline (*Damerov*, Ber. 27, 2232).

Homoisophthalic acid, m.p. 185° (*Komppa*, Ber. 36, 3611), and homoterephthalic acid, both sublime. *m*- and *p*-Cyanobenzyl cyanide, m.p. 88° and 100° (*Reinglass*, Ber. 24, 2416). In addition to the dinitrile of homoterephthalic acid, the two nitrile and the two amic acids, the two possible amidonitriles, and the diamide have also been prepared (*Fileti*, Gazz. 22, II, 389; 23, I, 433).

*o*-Hydrocinnamo-dicarboxylic acid, COOH[2]C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>COOH, m.p. 165°, is prepared by oxidising tetrahydro-β-naphthylamine with permanganate, or by reducing dihydro-isocoumarin-carboxylic acid, or *o*-carboxyphenyl-glycerolic-δ-lactone (*Bamberger*, Ber. 25, 888; 26, 1841). It gives α-hydrindone on dry distillation.

*o*-Cyanobenzylacetic ester, cyano-hydrocinnamic ester, CN[2]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>-CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>, m.p. 98°, is obtained by the action of cyanobenzyl chloride on acetoacetic ester or malonic ester in the presence of sodium ethylate, with subsequent rearrangement of the primary product (*Landsberger*, Ber. 31, 2885). It

gives α-hydrindone, C<sub>6</sub>H<sub>4</sub>  $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$  CH<sub>2</sub>, with conc. HCl.

**Phenylbutyric-*o*-carboxylic acid**,  $\text{COOH}[2]\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ , m.p. 139–140°, is obtained by acid hydrolysis of  $\alpha$ -tetralone- $\beta$ -oxalic ester (*Hückel*, Ber. 57, 1285).

(c) **AROMATIC DICARBOXYLIC ACIDS WITH THE TWO CARBOXYL GROUPS IN DIFFERENT SIDE-CHAINS.**

*o*-, *m*-, and *p*-Phenylenediacetic acids,  $\text{C}_6\text{H}_4(\text{CH}_2\text{COOH})_2$ , m.p. 150°, 170°, and 244° are obtained from the corresponding xylylene cyanides (*Oddo*, Gazz. 23, II, 337). The *o*-acid is also obtained by the oxidation of dihydronaphthalene. Its calcium salt gives  $\beta$ -hydrindone on distillation (*Bamberger*, Ber. 26, 1833). *o*-, *m*-, and *p*-Xylylene cyanides,  $\text{C}_6\text{H}_4(\text{CH}_2\text{CN})_2$ , m.p. 60°, 30°, and 98°, are obtained from the corresponding xylylene dibromides by the action of hot aqueous-alcoholic KCN. When reduced, they give  $\beta$ , $\beta'$ -diamino-diethyl-benzenes; the *o*-cyanide also gives  $\beta$ -amino- $\beta$ -methyl-hydrindone, and the *m*-cyanide, a monoamine. The quaternary ammonium iodide of the latter (m.p. 236°) gives an unsaturated bicyclic hydrocarbon,  $\text{C}_{10}\text{H}_{10}$ , b.p. 62–63° (18 mm.), which readily resinifies (*Braun*, Ber. 49, 2642; 53, 98).

*o*-Phenylenecetic-propionic acid,  $\text{C}_6\text{H}_4(\text{CH}_2\text{COOH})[2](\text{CH}_2\text{CH}_2\text{COOH})$ , m.p. 139°, is produced by fission of the ring of  $\beta$ -hydroxy- $\alpha$ -naphthoic acid by means of sodium and amyl alcohol. The reaction is similar to that by which pimelic acid is obtained from salicylic acid (p. 356). Distillation of its calcium salt gives  $\beta$ -keto-tetrahydronaphthalene (*Einhorn*, Ann. 286, 257).

*o*-, *m*-, and *p*-Phenylene-dipropionic acid,  $\text{C}_6\text{H}_4(\text{CH}_2\text{CH}_2\text{COOH})_2$ , m.p. 161°, 146°, and 223°, are obtained from the xylylene-dimalonic acids (*Perkin*, Kipping, Ber. 19, 436; 21, 37). *p*-Phenylene-diisobutyric acid,  $\text{C}_6\text{H}_4(\text{CH}_2\text{CH}(\text{CH}_3)\text{COOH})_2$ , m.p. 169°, is obtained in a similar way from *p*-xylylene-dimethylmalonic acid (*Ephraim*, Ber. 34, 2789). For *m*- and *p*-dicarboxylic acids of the formulae  $\text{C}_6\text{H}_4[(\text{CH}_2)_4\cdot\text{COOH}]_2$  and  $\text{C}_6\text{H}_4[(\text{CH}_2)_6\cdot\text{COOH}]_2$  see *Ruzicka*, Helv. 15, 1220.

## 2. Aldehydo-dicarboxylic Acids

2-Aldehydo-isophthalic acid, m.p. 176°, is obtained by heating 2,6-dicarboxy-phenyl-glyoxylic acid (*Jungbluth*, Ber. 26, 1767; *Liebermann*, Ber. 30, 695). 5-Aldehydo-4-hydroxy- and 5-aldehydo-2-hydroxy-isophthalic acids are produced by the action of chloroform and caustic potash on the corresponding hydroxy-isophthalic acids.

## 3. Aromatic Tricarboxylic Acids

The three isomeric benzene tricarboxylic acids are known.

**Trimesic acid**, 1,3,5-benzene tricarboxylic acid, m.p. 360°, sublimes at 200°. It can be obtained: 1. By the oxidation of mesitylene with permanganate (*Ullmann*, Ber. 36, 1799), or by the oxidation of mesitylenic or uvitic acid with chromic acid; 2. from mellitic acid by heating it with glycerol, or from hydro- or isohydro-mellitic acid by the action of sulphuric acid; 3. synthetically, it is made from benzene-1,3,5-trisulphonic acid by heating with potassium cyanide and hydrolysing the resulting tricyanobenzene. Trimesic acid and its esters are obtained by the condensation of some aliphatic substances. The following are examples: (1) polymerisation of propiolic acid gives trimesic acid; (2) the monomethyl ester is obtained by the action of caustic potash on coumalic acid (*Pechmann*, 1891); (3) the triethyl ester is obtained from formylacetic ester; (4) *Reformatsky's* synthesis of trimesic ester from ethyl formate and ethyl halogenoacetates by means of zinc (C. 1898, II, 472) probably occurs with the intermediate formation of formyl-acetic ester. **Trimethyl ester**, m.p. 143°; **triethyl ester**, m.p. 133°.

**Trimellitic acid**, 1,2,4-benzene-tricarboxylic acid, melts at 216°, with decomp. into water and trimellitic anhydride,  $\text{COOH}[4]\text{C}_6\text{H}_3(\text{CO})_2\text{O}$ , m.p. 158°. It is obtained, together with isophthalic acid, by heating hypopyromellitic acid with sulphuric acid, by oxidation of xylidinic acid with permanganate, and from amino-terephthalic acid (*Ahrens*, Ber. 19, 1635). The most convenient method of preparation is by oxidising colophony resin with nitric acid; isophthalic acid is formed at the same time (*Wegscheider*, Mo. 31, 1253).

**Hemimellitic acid**, 1,2,3-benzene-tricarboxylic acid, melts at 190°, being converted into its anhydride. It is obtained by heating hexahydromellitic acid, and by the oxidation of phenylglyoxyl-dicarboxylic acid, which is obtained by oxidation of naphthalic acid with permanganate. **Trimethyl ester**, m.p. 101–102° (*Meyer*, Ber. 50, 452); **triethyl ester**, m.p. 39° (*Graebe*, Ann. 290, 212; *Ephraïm*, Ber. 31, 2084).

**HYDROXY-TRICARBOXYLIC ACIDS** have been obtained from sulphotricarboxylic acids. **Hydroxy-trimesic acid**, and **hydroxy-trimellitic acid** (*Jacobsen*, Ann. 206, 204). **Hydroxy-methyl-trimesic** and **dihydroxy-trimesic esters** have been obtained by the condensation of ethoxyacetoacetic ester and ethoxymalonic ester with sodio-acetone-dicarboxylic ester (*Errera*, Ber. 32, 2776). **Hydroxy-trimellitic acid**, see *Jacobsen*, Ber. 16, 192. **Methyl-hydroxy-hemimellitic acid**, *cochinealic acid*,  $(\text{HO})[6](\text{CH}_3)[4]\text{C}_6\text{H}[1,2,3](\text{COOH})_3$ , m.p. 224–225°, is a degradation product of cochineal (*Liebermann*, Ber. 30, 1773).

**Dihydroxy-phenyl-acetic-dicarboxylic ester**, obtained in the condensation of sodio-acetone-dicarboxylic ester—an example of the formation of the benzene ring from aliphatic compounds—is dealt with under the hydro-aromatic compounds (Vol. II, p. 148).

#### 4. Aromatic Tetracarboxylic Acids

The three isomeric benzene tetracarboxylic acids are known. They give tetrahydrobenzene-tetracarboxylic acids on reduction (see Vol. II, p. 149).

**Pyromellitic acid**, 1,2,4,5-benzene-tetracarboxylic acid,  $\text{C}_6\text{H}_2(\text{COOH})_4 + 2\text{H}_2\text{O}$ , melts when anhydrous at 273–275°, and decomposes into water and the dianhydride of the acid; the latter is also formed when mellitic acid, or better its sodium salt, is distilled with sulphuric acid (*Meyer*, Mo. 35, 391). The acid itself is formed by the oxidation of durol or durylic acid with permanganate, and also from octahydro-anthracene through the two possible non-separable diphthalonic acids (*Braun*, Ber. 57, 681). It is also obtained from pine charcoal by the action of sulphuric acid (*Philippi*, Org. Synth. 10, 90), and it is a degradation product of *podophyllin* (Vol. II). It can be obtained synthetically by the action of caustic potash on  $\alpha,\beta$ -dibromo-glutaric acid (*Feist*, Ber. 44, 135). The dianhydride has the formula  $\text{O}(\text{CO})_2\text{C}_6\text{H}_2(\text{CO})_2\text{O}$ ; tetraethyl ester, m.p. 54°. **Dinitro-** and **diamino-pyromellitic tetraethyl ester**, m.p. 130° and 134°. The diamino-ester is oxidised by nitric acid to

**Quinone-tetracarboxylic ester**,  $(\text{O})_2\text{C}_6(\text{COOC}_2\text{H}_5)_4$ , m.p. 140°, lemon-yellow needles. It is odourless, and readily sublimes. It is reduced by zinc dust and acetic acid to

**Hydroquinone-tetracarboxylic ester**,  $(\text{HO})_2\text{C}_6(\text{COOC}_2\text{H}_5)_4$ , m.p. 127°, which forms bright yellow needles. This compound can also be obtained by the action of iodine on sodio-acetone-dicarboxylic ester (*Pechmann*, Ber. 30, 2570), and can be reduced to *p*-diketo-cyclohexane-tetracarboxylic ester (*Nef*, Ann. 237, 25).

**Mellophanic acid**, 1,2,3,4-benzene-tetracarboxylic acid, m.p. 241° with anhydridisation. *Bamford* and *Simonsen* (J. 97, 1904) have prepared it by oxidising 1,2,3,4-tetramethyl benzene with permanganate, and also by oxidising 1,4-dimethyl-naphthalene with nitric acid; it is a degradation product of *picrotoxine* (Vol. II, p. 491).

**Prehnitic acid**, 1,2,3,5-benzene-tetracarboxylic acid,  $\text{C}_6\text{H}_2(\text{COOH})_4 + 2\text{H}_2\text{O}$ , melts when anhydrous at 252° with anhydridisation. It is formed, together with mellophanic and trimesic acids, on heating hydro- or isohydro-mellitic acid (Vol. II, p. 149) with sulphuric acid, and by the oxidation of either 1,2,3,5-tetramethylbenzene with permanganate, or mesitylene-carboxylic acid (p. 293) with nitric acid (*Bamford*, *Simonsen*, J. 97, 1904). The salts of this acid form crystals which resemble the mineral *prehnite*. The tetramethyl ester melts at 133–135°.

### 5. Aromatic Pentacarboxylic Acids

**Benzene-pentacarboxylic acid**,  $C_6H(COOH)_5$ , +  $6H_2O$ , decomposes on melting. It is obtained by the oxidation of pentamethyl benzene (p. 47) with permanganate (*Friedel, Crafts*, Ann. ch. ph. [6], 1, 449), by the action of concentrated sulphuric acid on charcoal (*Verneuil*, C.r. 152, 1340), and from tetrahydronaphthalene, or "tetralin," through the *ali-2-ethyl* compound, condensing this with diethyl-malonyl chloride, followed by oxidation, *etc.* (*Fleischer*, Ber. 56, 228). Fischer showed the presence of benzene pentacarboxylic acid in the products of oxidation under pressure of Willstätter's lignin at 200° in the presence of sodium carbonate solution. It is also a degradation product of podophyllin (Vol. II, p. 492). The pentamethyl ester melts at 150°.

### 6. Aromatic Hexacarboxylic Acids

**Mellitic acid**,  $C_6(COOH)_6$ , m.p. 288°, decomposing into water, carbon dioxide, and pyromellitic anhydride. Its aluminium salt is the mineral "honeystone" which is found in deposits of lignite, as a honey-coloured crystalline substance. It crystallises in four-sided pyramids (*Claus*, Ber. 10, 566). The formation of mellitic acid by the action of fuming nitric acid on charcoal or graphite, discovered by *Dickson* (Proc. 1898, 163), or by treating charcoal with alkaline permanganate (*Meyer*, Mo. 35, 163; Ber. 63, 2010), has already been mentioned (p. 26). It is formed when carbon or lamp-black pressed into rods is used as an anode in an electrolytic cell (*Bertoli*, Gazz. 13, 22; Ger. Pat. 318,200) and when hexamethyl-benzene is oxidised with permanganate. Since hexamethyl-benzene can be obtained synthetically, the last reaction serves for the synthesis of mellitic acid. Another synthesis (*Philippi*, Mo. 42, 5) starts with mesitylene, into which two acetyl groups are introduced; these are reduced to ethyl, and a third acetyl group is then introduced. Finally, the product is vigorously oxidised by nitric acid. *Lippmann* has detected it in industrial sugar sludge (Ber. 50, 236).

Mellitic acid crystallises in slender needles with a silky lustre. It readily dissolves in water or alcohol. It is very stable, and is unaffected by acids or chlorine or bromine, even when boiling. When distilled with lime it gives benzene. It condenses with phenols giving the coloured product mellitheine (*Meyer*, Ber. 63, 2010).

**History.**—*Klaproth* (1799) discovered mellitic acid by boiling honeystone with water for a long time. Its constitution remained unknown until *Baeyer*, in 1870, showed that it gave benzene when distilled with lime, and reduced it to hexahydromellitic acid, thus proving it to be benzene hexacarboxylic acid (Ann. Suppl. 7, 1).

**Anhydrides.**—When warmed with  $SOCl_2$ , a dianhydride, decomposing at about 300°, is formed. With acetyl chloride at 160° an infusible trianhydride is formed (*Meyer*, Mo. 35, 513). **Salts and esters:** The barium salt,  $C_6(COO)_2Ba_2$  +  $3H_2O$ , is insoluble in water. *Methyl* and *ethyl* esters melt at 187° and 73°.

**CHLORIDE**,  $C_6(COCl)_6$ , m.p. 190°. **Mellimide**, or **paramide**,  $C_6[(CO)_2NH]_3$  [?], is obtained by the dry distillation of the ammonium salt. It is a white, amorphous powder, insoluble in water or alcohol, which is converted into the triammonium salt of mellitic acid when heated with water to 200°. When treated with alkalis, mellimide is converted into *p-euchronic acid*,  $C_6[(CO)_2NH]_2[1,4]-(COOH)_2$ , which forms colourless prisms, and exists in mono-, di-, and tri-molecular forms, according to the conditions of preparation (*Mumm*, Ann. 411, 244). When heated with water to 200°, *euchronic acid* hydrolyses to give mellitic acid. Nascent hydrogen reduces it to a dark blue substance, called *euchrone*, which, on

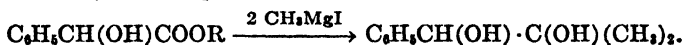
standing in the air, is reconverted into the colourless euchronic acid. It dissolves in alkalis giving a dark red solution.

### (3) AROMATIC POLY-ALCOHOLS, WITH MORE THAN ONE HYDROXYL GROUP IN A SIDE-CHAIN AND THEIR OXIDATION PRODUCTS

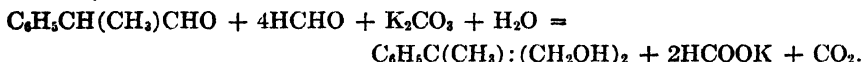
Among the aromatic poly-alcohols which contain hydroxyl groups attached to different carbon atoms in the same side-chain, the glycols, and their oxidation products, are at present the only group that has been thoroughly studied. Alcohols with more than two hydroxyl groups, and their oxidation products, will, therefore, not be described as separate groups, but will be dealt with in connection with the related glycols and their oxidation products.

#### 1. Phenyl-glycols and Phenyl-glycerol

**PHENYL-GLYCOLS** are formed: (1) by the action of potassium carbonate or baryta on the dibromides or bromohydrins of the olefine-benzenes; (2) by the gentle oxidation of olefine-benzenes with permanganate; (3) by nuclear synthesis by the action of alkyl magnesium halides on esters of aromatic hydroxy-acids and hydroxy-ketones, for example:



(4) Diprimary glycols are obtained by the action of formaldehyde and potassium carbonate solution on the aldehydes of the type  $\text{Ar} \cdot \text{CH}(\text{Alk}) \cdot \text{CHO}$  (Fournneau, Bull. 47, 858):



The  $\alpha$ -phenyl-glycols,  $\text{Ar} \cdot \text{CHOH} \cdot \text{C}(\text{OH})\text{RR}'$  exist in two stereoisomeric forms, according to the order in which the two substituents are introduced (Tiffeneau, C.r. 178, 1724).

When heated with dilute sulphuric acid, the 1,2-phenyl glycols lose water, and form aldehydes or ketones. Primary-secondary, and primary-tertiary glycols give aldehydes without rearrangement, while di-secondary and secondary-tertiary glycols either become ketones without rearrangement, or aldehydes with a migration of the phenyl group (Tiffeneau, Ann. ch. ph. [8], 10, 322; Bull. 49, 1595, 1617; cf. pp. 265, 266, 400).

**Phenyl-glycol**, *styrolene alcohol*,  $\text{C}_6\text{H}_5\text{CH}(\text{OH}) \cdot \text{CH}_2\text{OH}$ , m.p.  $67^\circ$ , b.p.  $273^\circ$ , is obtained by the action of potassium carbonate solution on styrol dibromide. It is converted into *benzoyl-carbinol*, and *benzoyl-formic acid* when oxidised with nitric acid. When warmed with dilute sulphuric acid it gives phenyl-acetaldehyde. Under the action of 65% sulphuric acid, two molecules condense to give  $\beta$ -phenyl-naphthalene (p. 613). When heated with caustic potash it is reduced to *phenyl-methyl-carbinol* (p. 252) (Palfray, C.r. 193, 941).

*Methylene ether*, b.p.  $218^\circ$ , is obtained from phenyl-glycol and formaldehyde (Hess, Ber. 32, 568). **Phenyl- $\omega$ -nitroethanol**,  $\text{C}_6\text{H}_5\text{CHOH} \cdot \text{CH}_2\text{NO}_2$ , b.p.  $163$ – $165^\circ$  (15 mm.), is obtained by condensing benzaldehyde with nitromethane under the influence of sodium methylate at temperatures below  $8^\circ$ . On warming it gives  $\omega$ -nitrostyrene (p. 444). *Methyl ether*, b.p.  $140$ – $141^\circ$  (15 mm.) (Rosenmund, Ber. 46, 1034). For ring-substituted homologues see Ger. Pat. 247,817.

**sym-Phenylmethyl-glycol**,  $\text{C}_6\text{H}_5\text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_3$ ,  $\alpha$ -modification, m.p.  $57^\circ$ ,  $\beta$ -modification, m.p.  $93^\circ$ . This glycol occurs in two forms, like hydrobenzoin. They are obtained from the corresponding dibromide (from *n*-propyl benzene). Both forms give phenyl-acetone when boiled with dilute sulphuric acid, and phenylmethyl-glyoxal when oxidised with nitric acid (Zincke, Ber. 43, 849).

**as-Phenylmethyl-glycol**,  $\text{C}_6\text{H}_5(\text{CH}_3)\text{COH} \cdot \text{CH}_2\text{OH}$ , m.p.  $41^\circ$ , b.p.  $161^\circ$  (26 mm.), is made by methods 1 and 3. When warmed with dilute sulphuric acid it gives hydratropic aldehyde (Tiffeneau, Ann. ch. ph. [8], 10, 322).

**1-Phenyl-2,3-propylene-glycol**,  $C_6H_5CH_2 \cdot CH(OH) \cdot CH_2OH$ , b.p.  $163^\circ$  (12 mm.), and **1-phenyl-3,4-butylene-glycol**,  $C_6H_5CH_2 \cdot CH_2 \cdot CH(OH) \cdot CH_2(OH)$ , b.p.  $178^\circ$  (14 mm.), are obtained from glycerol- $\alpha$ -monochlorhydrin by the action of phenyl- and benzyl-magnesium bromide, respectively (Ger. Pat. 164,883; Grignard, Ann. ch. ph. [8], 10, 23).

*sym*-**Dimethyl-, methyl-ethyl-, and diethyl-phenyl-glycol**,  $C_6H_5CH(OH) \cdot C(OH)R_2$ , m.p.  $63^\circ$ ,  $85^\circ$ , and  $89^\circ$ , respectively, are made by method 3. Under the action of conc. sulphuric acid, methyl-ethyl-phenyl-glycol is transformed into 3-phenylpentanone-2,  $C_6H_5CH(C_2H_5)COCH_3$ , an ethyl group having migrated. When heated with 8% sulphuric acid, all three glycols suffer a "phenyl migration," being transformed into dimethyl-, methyl-ethyl-, and diethyl-phenyl-acetaldehyde, respectively (Tiffeneau, Bull. 33, 735; Ann. ch. ph. [8], 16, 237). **2-Phenyl-trimethylene-glycol**,  $C_6H_5CH(CH_2OH)_2$ , b.p.  $145^\circ$  (12 mm.), is obtained from styrene and formaldehyde. *Diacetate*, b.p.  $175^\circ$  (12 mm.) (Prins, Weekblad, 14, 932). **2-Phenyl-2-methyl-trimethylene-glycol**,  $(C_6H_5)(CH_3)C:(CH_2OH)_2$ , m.p.  $87^\circ$ , is obtained from hydratropaldehyde by method 4 (Fournneau, Bull. 47, 858).

**1-Phenyl-1,3-butylene-glycol**,  $C_6H_5CHOH \cdot CH_2CHOH \cdot CH_3$ , b.p.  $168-169^\circ$  (13 mm.), is obtained from benzoyl-acetone by reduction with sodium and ethyl alcohol (Bauer, C.r. 154, 1092). **1-Phenyl-1,4-butylene-glycol**,  $C_6H_5CHOH \cdot CH_2CH_2CH_2OH$ , m.p.  $75^\circ$ , is obtained from benzoyl-propionaldehyde (p. 408) and from benzoyl-propyl-alcohol by reduction. **Phenyl-isopropyl-ethylene-glycol**,  $C_6H_5[CH(OH)]_2CH(CH_3)_2$ , m.p.  $81^\circ$ , is obtained from benzaldehyde and isobutylaldehyde by reduction. *m,p*-**Methylene-dioxybenzyl-ethylene-glycol**,  $[CH_2O_2][3,4]C_6H_5 \cdot CH_2CH(OH)CH_2(OH)$ , m.p.  $82^\circ$ , and *m,p*-**methylene-dioxyphenyl-methyl-ethylene-glycol**,  $(CH_2O_2)[3,4]C_6H_5 \cdot CH(OH) \cdot CH(OH) \cdot CH_3$ , m.p.  $101^\circ$ , is obtained from *safrol* (p. 452) and *iso-safrol*, by the action of permanganate (Wagner, Ber. 24, 3488), or lead tetraacetate (Criegee, Ann. 481, 300). Similarly, glycols are obtained from anethole, eugenol, and iso-eugenol, with m.p.  $116^\circ$ ,  $68^\circ$ , and  $88^\circ$ , respectively. The glycol formed from eugenol has been called hydrate-coniferyl alcohol; *Klason* (Ber. 63, 1548) has obtained it from pentosanes, and supposes it to be the parent substance of lignin.

**1-Phenyl-glycerol**, *stycerol*,  $C_6H_5CH(OH) \cdot CH(OH) \cdot CH_2(OH)$ , m.p.  $98-99^\circ$ , is obtained from cinnamyl alcohol dibromide,  $C_6H_5CHBr \cdot CHBr \cdot CH_2OH$ , by the action of permanganate on cinnamyl alcohol, or from  $\alpha$ -phenyl-glycidic alcohol,

$C_6H_5\overline{CH \cdot O} \cdot CH \cdot CH_2OH$  (waxy crystals, m.p.  $26.5^\circ$ ) by the action of 0.02 N hydrochloric acid at  $0^\circ$ .

**PHENYL-ALKYLENE OXIDES** are obtained from the halogen hydrins of the phenyl-glycols by treatment with alkali, from the phenyl-alkylenes by the action of perbenzoic acid or benzoperoxide (Levy, Bull. 49, 1830), and from the quaternary ammonium iodides of the aromatic amino-alcohols by the action of silver oxide (McKenzie, Ber. 65, 805). When they are heated, alone or with dilute sulphuric acid or zinc chloride, they undergo rearrangement into aldehydes or ketones (Fournneau, C.r. 141, 662). Alcoholic potash opens the oxide ring and alcohol is added on (McKenzie, loc. cit.).

**Styrene oxide**, phenyl-ethylene oxide,  $C_6H_5\overline{CH \cdot O} \cdot CH_2$ , b.p.  $191^\circ$ , is obtained by the action of caustic potash on phenyl-glycol-iodohydrin, or by the action of perbenzoic acid on styrene (Hibbert, Am. 47, 2240). With dilute acids it gives phenyl-acetaldehyde and diphenyl-diethylene oxide (Tiffeneau, C.r. 146, 697).

*as*-**Phenyl-methyl-ethylene oxide**,  $C_6H_5(CH_3)\overline{C \cdot O} \cdot CH_2$ , b.p.  $85-88^\circ$  (17 mm.), is converted into hydratropaldehyde on heating or by the action of dilute acids (Klages, Ber. 38, 1969).

*sym*-**Phenyl-methyl-ethylene oxide**,  $C_6H_5\overline{CH \cdot O} \cdot CH \cdot CH_3$ , b.p.  $93^\circ$  (15 mm.).

$\gamma$ -**Phenyl-propylene oxide**,  $C_6H_5CH_2\overline{CH \cdot O} \cdot CH_3$ , b.p.  $94-98^\circ$  (15 mm.) (Fournneau, C.r. 140, 1595).

Many ring-substituted phenyl-alkylene oxides have been prepared from vinyl- and propenyl-benzenes, such as anethole, *isosaftrol*, etc. (see p. 450), either by

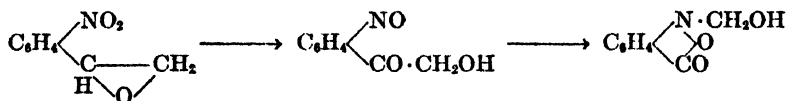


direct oxidation with hydrogen peroxide and alkali, or by way of the dibromide and  $\alpha$ -hydroxy- $\beta$ -bromides, by the action of alcoholic potash (*Weitz*, Ber. 54,

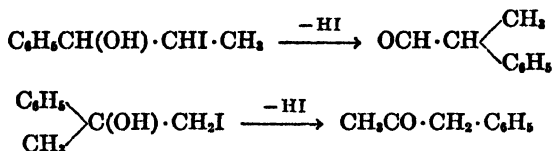
2327). **Anethole oxide**,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_4\text{CH}\cdot\text{O}\cdot\text{CH}\cdot\text{CH}_3$ , b.p.  $132^\circ$  (11 mm.);

**isosafrol oxide**,  $\text{CH}_3\text{O}[3,4]\text{C}_6\text{H}_3\text{CH}\cdot\text{O}\cdot\text{CH}\cdot\text{CH}_3$ , b.p.  $140\text{--}142^\circ$  (9 mm.).

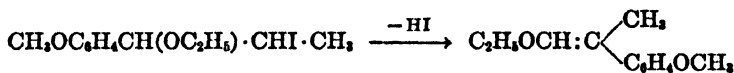
*o*-Nitrophenyl-ethylene oxide, m.p.  $65^\circ$  is the chief product of the action of diazomethane on *o*-nitro-benzaldehyde (*cf.* Vol. I, p. 351). In the presence of dilute acids it first isomerises to *o*-nitroso-benzoyl-carbinol (p. 405), and is then transformed into methylol-benzisoxazolone (*Arndt*, Ber. 61, 1107).



**HALIDE ESTERS OF THE PHENYL-GLYCOLS.** (a) *Halogenohydrins.* The reactions between the halogenohydrins of the phenyl-glycols and silver nitrate and mercuric oxide are of special interest. Caustic alkalis (as mentioned above) remove the halogen acid forming alkylene oxides, but silver nitrate and mercuric oxide remove the halogen acid and at the same time bring about a migration of the phenyl group, so that aldehydes or ketones are formed (*Tiffeneau*, Ann. ch. ph. [8], 10, 322; Bull. 49, 1595, 1617):



HI is probably removed from atoms attached to one and the same carbon atom. This is indicated by the fact that the iodohydrin ethers react with mercuric oxide in an exactly similar way to those of the glycols themselves, with migration of a phenyl group, and formation of phenyl-vinyl ethers (*Tiffeneau*, Bull. 1, 1205; C.r. 146, 29):



$\alpha$ -Phenylethylene- $\beta$ -iodohydrin,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\cdot\text{CH}_2\text{I}$ , b.p.  $148\text{--}152^\circ$  (13 mm.), decomposing into HI and acetophenone. It is obtained by the action of iodine and yellow mercuric oxide on styrene in aqueous-etheral solution. The isomeric  $\alpha$ -phenyl-ethylene- $\alpha$ -iodohydrin,  $\text{C}_6\text{H}_5\text{CHI}\cdot\text{CH}_2(\text{OH})$ , m.p.  $79^\circ$ , is obtained by the addition of HI to styrene oxide (C.r. 145, 811; 146, 697).

$\beta$ -Phenyl-propylene-glycol- $\alpha$ -chlorohydrin,  $\text{C}_6\text{H}_5(\text{CH}_2)\text{C}(\text{OH})\cdot\text{CH}_2\text{Cl}$ , b.p.  $124^\circ$  (17 mm.), is obtained by the action of phenyl magnesium bromide on chloroacetone, and of methyl magnesium iodide on  $\omega$ -chloro-acetophenone. It is also obtained by the addition of hypochlorous acid to isopropenyl-benzene. **Fromohydrin**, b.p.  $141^\circ$  (19 mm.). **Iodohydrin**, b.p.  $145^\circ$  (12 mm.) (*Tiffeneau*, Ann. ch. ph. [8], 10, 145).  $\gamma$ -Phenyl-trimethylene-glycol- $\alpha$ -chlorohydrin,  $\text{C}_6\text{H}_5\cdot\text{CHOH}\cdot\text{CH}_2\text{CH}_2\text{Cl}$ , b.p.  $142^\circ$  (20 mm.), is obtained by the action of phenyl magnesium bromide on  $\beta$ -chloropropionaldehyde. **Benzyl-glycol-chlorohydrin**,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ , b.p.  $153^\circ$  (27 mm.), is obtained by the action of phenyl magnesium bromide on epichlorohydrin (*Fourneau*, Bull. 1, 1227; 25, 364).

(b) *Dihalides.*—These are the addition products of the olefine-benzenes and halogens. The dibromides of olefine-phenols and their ethers recall the hydroxy-phenyl halides (pseudophenol halides, p. 339) in that the bromine atom in the  $\alpha$ -position to phenyl is remarkably mobile. When treated with aqueous acetone, sodium ethylate, potassium acetate, aniline, etc., it is readily replaced by the groups OH, OEt, OAc, NHPh, etc. (see also p. 450). A remarkable reaction occurs with concentrated nitric acid, when the  $\alpha$ -bromine atom migrates to the

nucleus and  $\alpha$ -ketones are formed. Thus, anethole bromide (see below) gives  $(\text{CH}_3\text{O})\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CH}_3$  (Höring, Ber. 38, 3458).

Styrene dichloride,  $\alpha,\beta$ -dichloroethylbenzene,  $\text{C}_6\text{H}_5\text{CHClCH}_2\text{Cl}$ , is a liquid. Styrene dibromide, m.p.  $74.5^\circ$ . Anethole dibromide,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CHBr}\cdot\text{CHBr}\cdot\text{CH}_3$ , m.p.  $65^\circ$ . Isosafrol dibromide,  $\text{CH}_2(\text{O})_2\text{C}_6\text{H}_4\text{CHBr}\cdot\text{CHBrCH}_3$ , m.p.  $87^\circ$  (Wallach, Ber. 28, 2719).

**PHENYL- AND HYDROXYPHENYL-HYDROXYALKYL AMINES.** These compounds have acquired great importance since it was discovered that substances of considerable physiological interest, such as ephedrine and especially *adrenaline*, belong to this class. They are obtained: (1) by the action of amines on phenyl-glycol halogenohydrins; (2) from phenyl-ketols or phenyl-paraffin diketones by reduction in the presence of amines; (3) from aromatic isonitroso-ketones, amino-ketones, hydroxy-nitriles, and keto-nitriles by reduction; (4) from phenyl-haloalkyl-ketones by reduction in the presence of amines; (5) by the reduction of aromatic nitro-alcohols, obtained by the action of nitromethane and alkali on aromatic aldehydes. A special method for the preparation of hydroxy-alkyl amines with a primary OH group consists of treating diprimary glycols with a solution of hydrogen bromide in glacial acetic acid, and acting on the resulting bromo-acetates,  $\text{Ar}\cdot\text{C}(\text{CH}_3)(\text{CH}_2\text{Br})\cdot\text{CH}_2\text{OCOCH}_3$ , with primary or secondary amines (Fournéau, Bull. 47, 858).

The reduction is usually carried out with sodium amalgam, or electrochemically.

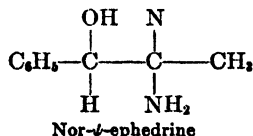
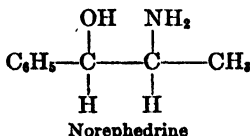
A number of compounds belonging to this group are known in several stereoisomeric forms, and in optically active forms.

A considerable volume of literature on this subject has grown since the pharmacological importance of the group was discovered.

**Methylamino-phenyl-carbinol**, *methylamino-benzyl alcohol*,  $\text{C}_6\text{H}_5\text{CHOH}\cdot\text{NHCH}_3$ , m.p.  $180^\circ$  (decomp.), is obtained from mandelo-nitrile by reduction with stannous chloride or zinc dust in dilute alcoholic solution (Wood, J. 127, 95).

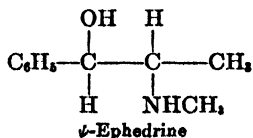
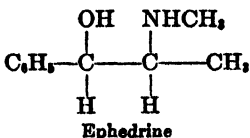
**1-Amino-2-phenyl-ethan-2-ol**, phenyl-hydroxyethyl amine,  $\text{C}_6\text{H}_5\text{CHOH}\cdot\text{CH}_2\text{NH}_2$ , m.p. about  $40^\circ$ ; its hydrochloride softens at  $136^\circ$ , and melts at  $211^\circ$ . The picrate melts at  $154^\circ$ . The substance is obtained by reduction of mandelo-nitrile with sodium amalgam (Ger. Pat. 193,634), or from  $\omega$ -amino-acetophenone hydrochloride or hydrobromide (Mannich, Arch. Pharm. 253, 181).

**2-Amino-1-phenyl-propan-1-ol**, *norephedrine*, *mydriatine*,  $\text{C}_6\text{H}_5\text{CHOH}\cdot\text{CH}(\text{NH}_2)\text{CH}_3$ , occurs in two stereoisomeric forms, each of which can exist in a racemic and two optically active forms. The stereoisomerides have the following constitutions:



Dextro-rotatory  $\psi$ -norephedrine is found together with ephedrine and its homologues in the Chinese drug *ma-huang*, obtained from *Ephedra vulgaris* (McKenzie, Ber. 65, 799). It has been prepared synthetically by reducing phenylnitropropanol (which gives both stereoisomers, Kanao, Pharm. Japan, 48, 122), isonitroso-propiophenone (Coles, Am. 51, 2269), or the oxime obtained by the action of methyl magnesium iodide on *d*-mandelic amide (Leithe, Ber. 65, 664). The melting points are: norephedrine: (active)  $50-52^\circ$ ; (*d,l*)  $104-105^\circ$ ; hydrochloride: (active)  $171-172^\circ$ ; (*d,l*)  $183^\circ$ ; nor- $\psi$ -ephedrine: (active),  $77.5-78^\circ$ ; (*d,l*),  $71^\circ$ . On methylation, the stereoisomers give ephedrine and  $\psi$ -ephedrine, respectively.

**2-Methylamino-1-phenyl-propan-1-ol**, *ephedrine*,  $\text{C}_6\text{H}_5\text{CHOH}\cdot\text{CH}(\text{NHCH}_3)\cdot\text{CH}_3$ , occurs in the stereoisomeric forms with the constitutions:



(Schmidt, Arch. Pharm. 253, 52; Freudenberg, Ann. 510, 223). *l*-Ephedrine and *d*- $\psi$ -ephedrine are found in the Chinese drug *ma-huang*. Melting points: Ephedrine: active, 40–50°; *d,l*, 75°; hydrochloride, active, 216–217°; *d,l*, 187–188°.  $\psi$ -Ephedrine: active, 117–118°; *d,l*, 118°; hydrochloride, active, 182°; *d,l*, 164°. The "normal" and pseudo-compounds are separated by making use of the different solubilities of their hydrochlorides in alcohol. The racemic bases are resolved into their antipodes by means of the *l*-tartrates (Kanao, loc. cit.).

The two forms of ephedrine have been obtained synthetically as follows: from phenyl-acetyl carbinol, acetyl-benzoyl (Br. Pat. 336,412), bromo-propiophenone (Ger. Pat. 472,466), and from 1-phenyl-1-methoxy-2-bromo-propane (*Späth*, Ber. 58, 1268). The physiological action of ephedrine is similar to that of adrenaline. It causes an increase in the blood-pressure owing to contraction of the blood vessels. It is a mydriatic, and it excites the sympathetic nervous system (Chen, J. Pharm. Ther. 24, 339).

When heated with acetic anhydride, ephedrine is converted into (acetyl)- $\psi$ -ephedrine (Kanao, Pharm. Japan, 1927 and 1928); and conversely  $\psi$ -ephedrine is converted into ephedrine by heating with hydrochloric acid (*Späth*, Mo. 41, 310). Both hydrochlorides decompose when heated in the dry state to give methylamine and propiophenone (Schmidt, Arch. Pharm. 247, 141). With benzaldehyde, ephedrine forms 2,5-diphenyl-3,4-dimethyl-tetrahydro-oxazole, m.p. 93.5° (Stratton, J. 1932, 1133). For the halides of active ephedrine and  $\psi$ -ephedrine, see Gossner, C. 1933, II, 2978; and for hexahydro-ephedrine and  $\psi$ -ephedrine, racemic and optically active, and for the configuration of the two bases, see Skita, Ber. 66, 974, 983.

Many homologues of ephedrine and related compounds have been prepared by varying the starting materials. Ring-substituted phenyl-ketols, the derivatives of hydroxy- and methoxy-aldehydes, give compounds substituted in the phenyl residue; higher phenyl-alkyl ketones give derivatives with longer carbon chains; derivatives with ethyl, phenyl, and benzyl attached to the nitrogen have also been prepared. One methyl-ephedrine is found in *Ephedra vulgaris* (Skita, Ber. 65, 799). For the syntheses of these compounds, see Koller, Mo. 47, 397; Hyde, Am. 50, 2218; Arch. Pharm., 271, 51; U. S. Pat 1,799,110; Ger. Pats. 524,806 and 525,839.

The following are isomeric with ephedrine: 3-methylamino-2-phenyl-propan-2-ol,  $C_6H_5(CH_3)\dot{C}(OH)CH_2NHCH_3$ , b.p. 137° (38 mm.), and 3-methylamino-1-phenyl-propan-2-ol,  $C_6H_5\dot{C}H_2CH(OH)CH_2NHCH_3$ , b.p. 148° (22 mm.), obtained by method 1 (Fourneau, J. pharm. chim. 20, 481). 1-Methylamino-1-phenyl-propan-2-ol,  $C_6H_5C(NHCH_3)CH(OH)CH_3$ , is an oil, obtained from  $\alpha$ -bromo-benzyl-methyl ketone and methylamine, followed by reduction; hydrochloride, m.p. 191–193° (Ende, Arch. Pharm. 249, 354).

1-Phenyl-2-amino-butan-1-ol,  $C_6H_5\dot{C}H(OH)CH(NH_2)C_2H_5$ , m.p. 81°; 1-phenyl-2-amino-pentan-1-ol,  $C_6H_5\dot{C}H(OH)CH(NH_2)C_3H_7$ , m.p. 70–71°, and other homologues of this series have been obtained from the isonitroso-compounds of phenyl-alkyl ketones (Hartung, Am. 52, 3317).

2-Methylamino-1-*p*-hydroxyphenyl-ethan-1-ol, *sympathol*,  $(HO)[4]C_6H_4\dot{C}H(OH)\cdot CH_2NHCH_3$ , m.p. 184–185°, is obtained from anisaldehyde cyanhydrin (Arch. Pharm. 269, 606). 2-Amino-1-*m,p*-dihydroxy-phenyl-ethan-1-ol, *nor-adrenaline*, *arteranol*,  $(HO)_2[3,4]C_6H_3\dot{C}H(OH)CH_2NH_2$ , is a white crystalline powder, m.p. 191° (decomp.), obtained by the reduction of amino-aceto-catechol, or from protocatechu-aldehyde-cyanhydrin (Ger. Pat. 193,634) or from  $\omega$ -amino-3,4-dihydroxy-acetophenone hydrochloride (Arch. Pharm. 269, 603).

Adrenaline, *suprarenin*, *epinephrin*, 1-(*m,p*-dihydroxy-phenyl)-2-methylamino-ethan-1-ol,  $(HO)_2[3,4]C_6H_3[1]\dot{C}H(OH)\cdot CH_2NHCH_3$ , was the first hormone to be isolated from animal organs (1901). See Vol. II, p. 579.

In addition to the synthesis given there, adrenaline can be obtained from veratraldehyde as follows—the aldehyde is converted into the cyanhydrin, then into the ketonitrile, then the amino-methyl-ketone  $Ar\cdot CO\cdot CH_2NH_2$ , then the *p*-toluolsulphonic compound, *N*-methylation, and reduction with decomposition (Arch. Pharm. 269, 587). Homologues and analogues of adrenaline have been prepared from aromatic aldehydes through the benzoyl cyanides (*ibid.*, 583).

Certain oxidation products obtained from adrenaline, of unknown constitution, are catalysts for oxidation processes, *e.g.*, for the deamination of amino-acids (*Bliz*, *Skand. Physiol.* **56**, 131). A number of adrenaline derivatives have a physiological action similar to that of adrenaline itself. Adrenaline-dimethyl ether,  $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}(\text{OH})\cdot\text{CH}_2\text{NHCH}_3$ , m.p.  $104^\circ$ , and adrenaline-methylene ether,  $\text{CH}_2(\text{O})_2\text{C}_6\text{H}_3\text{CH}(\text{OH})\cdot\text{CH}_2\text{NHCH}_3$ , m.p.  $96^\circ$ , are formed from the bromohydrins of the corresponding olefine-phenol ethers with methylamine (*Mannich*, *Arch. Pharm.* **248**, 127).

## 2. Phenyl-alcohol Aldehydes

Just as aldol is formed by the condensation of two molecules of acetaldehyde, nitrobenzaldehydes condense with acetaldehyde under the action of very dilute sodium hydroxide (2%) to form the corresponding aldols, the **nitrophenyl-hydracrylic-aldehydes**,  $\text{NO}_2\text{C}_6\text{H}_3\text{CH}(\text{OH})\cdot\text{CH}_2\text{CHO}$ , and these will add on another molecule of acetaldehyde. Dehydrating agents, such as acetic anhydride, convert them into nitro-cinnamic aldehydes (*Göhrling*, *Ber.* **18**, 719). Primary aldehydo-alcohols are obtained by the action of formaldehyde and caustic potash on phenylalkyl aldehydes (*Fourneau*, *Bull.* **47**, 850).

**$\alpha$ -Hydroxyphenyl-acetaldehyde**, *mandelic aldehyde*,  $\text{C}_6\text{H}_5\text{CHOHCHO}$ , is an unstable oil, which readily changes into benzoyl-carbinol (see below); semicarbazone, m.p.  $222^\circ$  (decomp.). It is prepared from styryl-urethane,  $\text{C}_6\text{H}_5\text{CH}:\text{CH}\cdot\text{NHCOOC}_2\text{H}_5$ , through its dihydroxy-derivative, which is added to boiling alcoholic sulphuric acid (*Kinkes*, *Rec.* **39**, 704).

***o*-Hydroxy-mandelic aldehyde**, ***o*-hydroxyphenyl-glycol-aldehyde**,  $\text{HO}[2]\text{C}_6\text{H}_3\text{CH}(\text{OH})\text{CHO}$ , m.p.  $64^\circ$ , has been obtained from *coumarone dichloride* (Vol. IV) by decomposing it with sodium acetate (*Stoermer*, *Ann.* **313**, 96).

**Benzyl-glycol-aldehyde**,  $\text{C}_6\text{H}_5\text{CH}_2\text{CHOH}\cdot\text{CHO}$ , m.p.  $51.5\text{--}52^\circ$ , is obtained by the action of barium carbonate on  $\alpha$ -bromohydrocinnamic aldehyde (*Danilov*, *Ber.* **63**, 2765). In acidic alcoholic solution it undergoes a transformation to phenyl-acetyl carbinol (p. 406).

**2-Phenyl-2-methyl-propan-1-ol-3-al**,  $\text{CH}_2\text{OH}\cdot\text{C}(\text{C}_6\text{H}_5)(\text{CH}_3)\text{CHO}$ , m.p.  $88\text{--}89^\circ$ , is obtained from hydratropic aldehyde (*Fourneau*, *Bull.*, **47**, 850). Its methyl ether, b.p.  $123\text{--}124^\circ$  is oxidised with silver nitrate (*Beaufour*, *Bull.* **27**, 148).

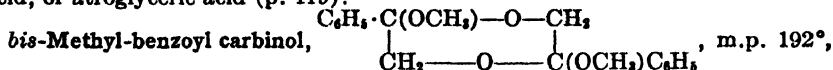
**Phenyl-glyceraldehyde**,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CHO}$ , is formed as a dimethyl-acetal, m.p.  $80^\circ$ , by the oxidation of cinnamic aldehyde acetal with permanganate; phenylhydrazone, m.p.  $170^\circ$  (*Fischer*, *Ber.* **31**, 1995). **Phenyl-tetrose**,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\cdot\text{CHO}$ , is a colourless syrup, formed by the reduction of phenyl-trihydroxy-butyric lactone (p. 421). Phenylhydrazone, m.p.  $154^\circ$ .

## 3. Phenyl-ketols

**Acetophenone alcohol**, **benzoyl carbinol**,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_2\text{OH}$ , m.p.  $73\text{--}74^\circ$ , hydrated,  $87^\circ$ , anhydrous, cryst. from ether. This compound is an oxidation product of phenyl-glycol, or can be obtained from its halides,  $\omega$ -chloro- and  $\omega$ -bromo-acetophenone (see below) by converting them into the acetate, which is then hydrolysed with sodium carbonate (*Plöchl*, *Ber.* **16**, 1290; *Stoermer*, *Ber.* **39**, 2294; *Madelung*, *Ber.* **65**, 935). It is also obtained from  $\omega$ -diazo-acetophenone by the action of dilute sulphuric acid, and from benzene and acetyl-glycolic chloride by the action of aluminium chloride (*Anschütz*, *Ann.* **368**, 89).

On distillation it decomposes with formation of benzaldehyde. Being a ketone, benzoyl carbinol forms crystalline compounds with alkali bisulphites, an oxime, m.p.  $70^\circ$ , with hydroxylamine, a phenylhydrazone, m.p.  $112^\circ$ , with phenylhydrazine, and the osazone of phenyl-glyoxal (p. 407). Like acetyl-carbinol it reduces ammoniacal silver nitrate even in the cold, forming benzaldehyde and benzoic acid; it also reduces alkaline copper solutions forming mandelic acid (p.

409). Nitric acid oxidises it to phenyl-glyoxylic acid (p. 422) (*Michael*, Ber. 14, 2100). It gives a cyanhydrin with HCN, which is the nitrile of  $\alpha$ -phenyl-glyceric acid, or atroglyceric acid (p. 419).



is formed by the action of methyl alcohol and hydrochloric acid on benzoyl carbinol (*Fischer*, Ber. 28, 1161). Benzoyl-carbinol acetate,  $\text{C}_6\text{H}_5\text{CO} \cdot \text{CH}_2\text{OCOCH}_3$ , m.p.  $49^\circ$ , b.p.  $270^\circ$ . Benzoate, m.p.  $117^\circ$ . Phenyl ether, m.p.  $72^\circ$ .

$\omega$ -Mercapto-acetophenone, phenacyl-mercaptan,  $\text{C}_6\text{H}_5\text{COCH}_2\text{SH}$ , m.p.  $23-24^\circ$ , is obtained by the action of phenyl-acyl bromide on sodium hydrogen sulphide. Keto-form, m.p.  $81^\circ$ , enol form, m.p.  $168-170^\circ$  (*Groth*, Ark. Kemi 9, 1). Much diphenacyl disulphide,  $(\text{C}_6\text{H}_5\text{COCH}_2)_2\text{S}_2$ , is formed at the same time. Diphenacyl sulphide,  $(\text{C}_6\text{H}_5\text{COCH}_2)_2\text{S}$ , m.p.  $77^\circ$ . Diphenacyl sulphoxide,  $(\text{C}_6\text{H}_5\text{COCH}_2)_2\text{SO}$ , m.p.  $98^\circ$ . Sulphone, m.p.  $120^\circ$  (*Fromm*, Ann. 394, 310; 399, 353).

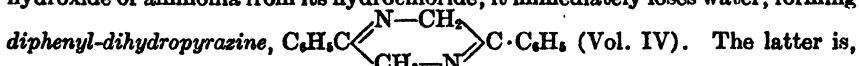
$\omega$ -Chloroacetophenone, phenacyl chloride,  $\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$ , m.p.  $59^\circ$ , b.p.  $247^\circ$ , is obtained by the chlorination of boiling acetophenone, by the action of hydrogen chloride on diazoacetophenone (see p. 405) (*Arndt*, Ber. 61, 1122), and from benzene and chloro-acetyl chloride in the presence of aluminium chloride.

$\omega$ -Bromoacetophenone, phenacyl bromide,  $\text{C}_6\text{H}_5\text{CO} \cdot \text{CH}_2\text{Br}$ , m.p.  $51^\circ$ , produces a vapour which strongly attacks the mucous membrane. It is obtained from acetophenone and bromine, from benzene by the action of bromo-acetyl bromide and aluminium chloride, by the action of hot water on dibromo-atrolactic acid (*Böttlinger*, Ber. 14, 1238), and when  $\alpha$ -bromo-styrene is allowed to stand in air, when a migration of the bromine atom takes place (*Dufraisse*, C.r. 172, 162). It adds on methyl-ethyl sulphide to form phenacyl-methyl-ethyl-sulphinium bromide,  $\text{C}_6\text{H}_5\text{COCH}_2\text{S}(\text{Me})(\text{Et})\text{Br}$ , which was the first compound with an asymmetric sulphur atom to be resolved into its optical antipodes by means of bromo-camphor-sulphonic acid. With excess alcoholic ammonia, phenacyl bromide gives diphenyl-dihydropyrazine (Vol. IV). With carboxylic amides and thioamides the  $\omega$ -halogeno-acetophenones give oxazole and thiazole derivatives (Vol. IV). Phenacyl bromide can be used for the identification of acids by means of their benzoyl carbinol esters. Those  $\omega$ -halogeno-acetophenones which contain hydroxyl groups in the O-position, such as gallo-chloroacetophenone,  $\text{C}_6\text{H}_2(\text{OH})_3\text{COCH}_2\text{Cl}$ , and  $\omega$ -bromoresacetophenone, easily pass into coumarone derivatives with loss of the halogen acid (*Brull*, Ber. 30, 299).

$\omega$ -Iodoacetophenone, phenacyl iodide,  $\text{C}_6\text{H}_5\text{COCH}_2\text{I}$ , m.p.  $30^\circ$ , is obtained by the action of potassium iodide on  $\omega$ -bromo- or  $\omega$ -chloroacetophenone (*Paal*, Ber. 32, 532). With silver nitrite it gives

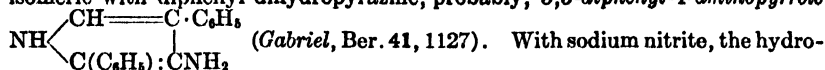
$\omega$ -Nitroacetophenone,  $\text{C}_6\text{H}_5\text{COCH}_2\text{NO}_2$ , m.p.  $108^\circ$ . This is also obtained from its dimethyl acetal,  $\text{C}_6\text{H}_5\text{C}(\text{OCH}_3)_2\text{CH}_2\text{NO}_2$ , which is itself obtained from phenyl-bromo-nitro-ethylene,  $\text{C}_6\text{H}_5\text{CH}:\text{CBrNO}_2$ , by the action of alcoholic potash. It is also formed when its oxime,  $\text{C}_6\text{H}_5\text{C}(\text{NOH}) \cdot \text{CH}_2\text{NO}_2$ , m.p.  $96^\circ$ , is hydrolysed. The oxime can be obtained from styrene-pseudonitrosite (p. 443) by boiling with alcohol (*Wieland*, Ber. 36, 2558). It dissolves in caustic potash to give the salt  $\text{C}_6\text{H}_5\text{COCH}:\text{NOOK}$ . It is reduced by stannous chloride to

$\omega$ -Aminoacetophenone,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2\text{NH}_2$ , a compound which is also obtained by the catalytic reduction at  $18^\circ$  of benzoyl cyanide (Arch. Pharm., 269, 581). It is only known in solution. Its hydrochloride, m.p.  $186-187^\circ$  (decomp.), is obtained by the reduction of isonitroso-acetophenone with tin and hydrochloric acid (*Rupe*, Ber. 28, 254), or by decomposing phthalimino-acetophenone,  $\text{C}_6\text{H}_4(\text{CO})_2\text{NCH}_2\text{COC}_6\text{H}_5$ , which is obtained by the action of  $\omega$ -bromoacetophenone on potassium phthalimide, or from phthalyl-glycyl chloride and benzene in the presence of aluminium chloride. Like the aliphatic  $\alpha$ -amino ketones,  $\omega$ -aminoacetophenone in the free state is unstable. When it is liberated by the action of sodium hydroxide or ammonia from its hydrochloride, it immediately loses water, forming



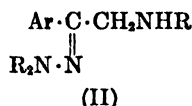
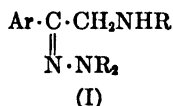
therefore, also obtained when ammonia acts on  $\omega$ -bromoacetophenone (see above). When it is heated with hydrochloric acid, the hydrochloride of  $\omega$ -amino-acetophenone is reformed. Diphenacyl-amine,  $(\text{C}_6\text{H}_5\text{COCH}_2)_2\text{NH}$ , m.p.  $75^\circ$ , is a by-product, formed in small amounts, when  $\omega$ -bromoacetophenone is acted upon

by ammonia. With excess of caustic soda,  $\omega$ -aminoacetophenone gives an oxygenated base,  $C_{10}H_{10}N_2O$ , m.p.  $131^\circ$ , which readily loses water and gives a base isomeric with diphenyl-dihydropyrazine, probably, 3,5-diphenyl-4-aminopyrrole



With sodium nitrite, the hydrochloride of  $\omega$ -aminoacetophenone gives  $\omega$ -diazooacetophenone, benzoyl-diazomethane,  $C_6H_5\text{COCHN}_2$ , m.p.  $50^\circ$ , which is also obtained by the hydrolysis of diazobenzoyl acetone with ammonia (p. 408).  $\omega$ -Diazooacetophenone, like the other diazo-ketones, is most conveniently prepared from benzoyl chloride and diazomethane (Arndt, Ber. 61, 1122, 1949; 66, 1012). On boiling with dilute sulphuric acid, diazoacetophenone is decomposed into nitrogen and benzoyl-carbinol. With iodine it gives  $\omega$ -diiodo-acetophenone,  $C_6H_5\text{COCHI}_2$ , and with potassium cyanide it gives the potassium salt of phenacyl-azo cyanide,  $C_6H_5\text{COCH}_2\text{N}:\text{NCN}$ , colourless crystals, m.p.  $72^\circ$  (decomp.). Sulphuric acid converts this salt into phenacyl-azo-carboxylamide,  $C_6H_5\text{COCH}_2\text{N}:\text{NCONH}_2$ , m.p.  $217^\circ$  (decomp.) (Wolff, Ann. 325, 141).

The hydrazones of the phenyl-acyl-amines,  $\text{Ar} \cdot \text{C} \cdot \text{COCH}_2\text{NH}_2$ , have all been obtained in a high melting *syn*-form (I), and a low melting *anti*-form (II), and in some cases, in a third form which is a molecular compound of (I) and (II):



$\omega$ -Methylamino- and -dimethylamino-acetophenone, and  $\omega$ -trimethylamino-acetophenone bromide,  $C_6H_5\text{COCH}_2\text{N}(\text{CH}_3)_3\text{Br}$ , are produced from phenacyl bromide by the action of mono-, di-, and trimethylamine.  $\omega$ -Acetophenone-aniline,  $C_6H_5 \cdot \text{CO} \cdot \text{CH}_2\text{NHC}_6\text{H}_5$ , m.p.  $93^\circ$ , is formed from  $\omega$ -bromoacetophenone and aniline (Miklan, Ber. 15, 2467), and readily condenses to  $\alpha$ -phenyl-indole (Vol. IV) (Fischer, Ber. 21, 1071; Staedel, Ber. 21, 2196; Culmann, Ber. 21, 2596).

*p*-Bromophenacyl bromide,  $\text{Br}[4]C_6H_4\text{COCH}_2\text{Br}$ , m.p.  $108\text{--}109^\circ$ , is obtained by the action of bromine on *p*-bromoacetophenone at  $20^\circ$  (Langley, Org. Synth. 9, 34, 129).

*o*-Nitroso-benzoyl carbinol, m.p.  $103\text{--}104^\circ$  (decomp.), is obtained from *o*-nitrophenyl-ethylene oxide by isomerisation in the presence of acids (p. 400) (Arndt, Ber. 60, 452; 61, 1113). *o*-Amino-benzoyl carbinol, m.p.  $98^\circ$ , is obtained by reducing *o*-nitroso-benzoyl carbinol with hydrazine, and is converted by dilute alkalis to indoxyl (Vol. IV) (Arndt, loc. cit.).

*p*-Aminobenzoyl carbinol,  $\text{NH}_2[4]C_6H_4\text{COCH}_2\text{OH}$ , m.p.  $165^\circ$ , is formed by rearrangement of *p*-acetamino-phenacyl chloride,  $\text{CH}_3\text{CONHC}_6H_4\text{COCH}_2\text{Cl}$ , m.p.  $212^\circ$ , obtained synthetically from acetanilide and chloroacetyl chloride in the presence of aluminium chloride (Kunckell, Ber. 33, 2644).

*o*-Nitro- $\omega$ -diazooacetophenone, m.p.  $105\text{--}106^\circ$ , is formed from *o*-nitrobenzoyl chloride by the action of diazomethane, and is decomposed by dilute acids containing oxygen into nitrogen and *N*-hydroxy-isatin (Vol. IV) (Arndt, Ber. 60, 1367).

$\alpha$ -Bromo-propiophenone,  $C_6H_5 \cdot \text{CO} \cdot \text{CHBrCH}_3$ , b.p.  $136\text{--}137^\circ$  (10 mm.), is obtained from  $\alpha$ -bromopropionyl chloride and benzene in the presence of aluminium chloride. With potassium acetate it gives the acetate of  $\alpha$ -hydroxy-propiophenone, b.p.  $125\text{--}126^\circ$  (14 mm.) (Auwers, Ber. 50, 1177).

$\alpha$ -Amino-propiophenone,  $C_6H_5 \cdot \text{CO} \cdot \text{CH}(\text{NH}_2)\text{CH}_3$ , hydrochloride m.p.  $183^\circ$ , is formed by the reduction of isonitroso-propiophenone, or from phthalyl-alanyl chloride (p. 387), benzene, and aluminium chloride. Like  $\omega$ -amino-acetophenone, the free base spontaneously loses water and becomes 2,5-dimethyl-3,6-

diphenyl-dihydropyrazine,  $C_6H_5\text{C} \begin{array}{c} \text{N}-\text{CH}(\text{CH}_3) \\ \diagup \quad \diagdown \\ \text{CH}(\text{CH}_3)-\text{N} \end{array} \text{CC}_6\text{H}_5$ . With hydrogen chloride, the latter gives a small quantity of the original amino ketone, but chiefly the isomeric compound,  $\alpha$ -amino- $\alpha$ -phenyl-acetone,  $C_6H_5\text{CH}(\text{NH}_2)\text{COCH}_3$ ,

which has also been obtained by reducing isonitrosophenyl-acetone (*Gabriel*, Ber. 41, 1146).

**prim.-Phenacetyl carbinol**,  $C_6H_5CH_2COCH_2OH$ , m.p. 47–48°, is produced by a thermo-catalytic rearrangement of phenyl-glycide alcohol,  $C_6H_5CH \cdot O \cdot CH \cdot$

$CH_2OH$  (*Weill*, C.r. 194, 977). **Phenyl-acetyl carbinol**,  $C_6H_5CH(OH)COCH_3$ , b.p. 205–207°, is obtained from  $\alpha$ -bromobenzyl-methyl ketone,  $C_6H_5CHBrCOCH_3$ , by the action of silver oxide, or through its acetate (*Carapelli*, Gazz. 33, II, 261). It can also be obtained from benzyl-glycol aldehyde by the action of slightly acidified alcohol (*Danilov*, Ber. 63, 2774).

**Benzoyl-methyl carbinol**,  $C_6H_5COCHOH \cdot CH_3$ , b.p. 250–252°, is obtained by the hydrolysis of its acetate (*Auwers*, Ber. 50, 1180), and is also formed by the spontaneous rearrangement of the isomeric phenyl-acetyl carbinol (see above). A biochemical synthesis of this compound from benzaldehyde and acetaldehyde under the action of the yeast enzyme carboligase, has been described by *Neuberg* (Bio. Z. 128, 610; 144, 44), but has been called in question by *Dirscherl* (Z. physiol. Chem. 201, 79).

**$\alpha$ -Benzylamino acetone**,  $C_6H_5CH_2CH(NH_2)COCH_3$ , hydrochloride, m.p. 127°, is obtained by the reduction of isonitroso-benzyl acetone (*Sonn*, Ber. 40, 4666).

*o*- and *p*-Nitrophenyl-hydracrylic ketones, m.p. 69° and 58°, correspond to the nitro-phenyl-hydracrylic aldehydes (p. 403). They are condensation products of *o*- and *p*-nitrobenzaldehydes and acetone, in the presence of very dilute caustic soda. When the *o*-ketone is boiled with water, or treated with an excess of sodium hydroxide, indigo is formed (*Baeyer*, 1883).

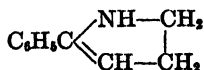
**2,4-Dihydroxybenzoyl carbinol**, *fisetol*,  $(HO)_2[2,4]C_6H_2COCH_2OH$ , m.p. 189°, is obtained from glycolic nitrile, chloro-carbonic ester and resorcinol (*Sonn*, Ber. 55, 2975), or from 2,4-diacetyl-resorcylic chloride and diazomethane, through the triacetate which is hydrolysed by alcoholic ammonia (*Nierenstein*, Am. 46, 2551). Its  $\omega$ ,4-dimethyl ether is a degradation product of *fisetin* (Vol. II, p. 445).

**$\alpha$ - $\omega$ -Chloroacetocatechol**,  $(HO)_2[3,4]C_6H_2[1]COCH_2Cl$ , m.p. 173°, is formed from catechol, chloracetic acid, and phosphorus oxychloride, or by a rearrangement of catechol monochloro-acetate (*Ott*, Ber. 59, 1071; *Rosenmund*, Ber. 61, 2601). With methylamine it gives  $\omega$ -methylamino-acetocatechol, *adrenalon*,  $(HO)_2[3,4]C_6H_2[1]COCH_2 \cdot NHCH_3$ , m.p. 229° (decomp.), which is also obtained from amino-dimethoxy-acetophenone by methylation, followed by preparation of the toluenesulphonic compound, and hydrolysis with hydrochloric acid (Arch. Pharm. 269, 587). Its action is similar to that of adrenaline, but 200 times weaker. Hydrochloride, m.p. 243° (decomp.). These two ketones are important intermediates in the synthesis of adrenaline (Vol. II, p. 579).

**$\beta$ -Methoxy-butyrophenone**,  $C_6H_5CCH_2CH(OCH_3)CH_3$ , b.p. 119–121° (8 mm.) is obtained from acetophenone and acetaldehyde in the presence of sodium methylate. It loses methyl alcohol easily, becoming propenyl-phenyl ketone (p. 460) (*Dufraisse*, Bull. 41, 843).

**$\omega$ -Benzoyl-butyl alcohol**,  $C_6H_5 \cdot CO \cdot (CH_2)_3 \cdot CH_2OH$ , m.p. 40° (*Kipping*, J. 57, 304).

**$\beta$ -Amino-propiofenone**,  $C_6H_5CO \cdot CH_2 \cdot CH_2NH_2$ ; hydrochloride, m.p. 128°. The latter is formed from  $\beta$ -phthalyl-alanyl chloride and benzene in the presence of aluminium chloride. Sodium hydroxide liberates the free base as an oil (*Gabriel*, Ber. 41, 244).  **$\gamma$ -Amino-butyrophenone**,  $C_6H_5CO \cdot CH_2 \cdot CH_2 \cdot CH_2NH_2$ , is unstable. As soon as it is formed it loses water and becomes 2-phenyl-pyrroline,



**$\delta$ -Amino-valerophenone**,  $C_6H_5COCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2NH_2$ , behaves similarly, becoming 2-phenyl-tetrahydro-pyridine. The compound itself is obtained from phthalimido-valeric acid.  **$\epsilon$ -Amino-caprophenone**,  $C_6H_5CO(CH_2)_4CH_2NH_2$ , hydrochloride, m.p. 154°, on the other hand, shows no tendency to lose water. The free base is an oil with a peculiar smell, volatile with steam (*Gabriel*, Ber. 41, 244, 513, 2014).

**Triphenacyl-methylamine**,  $(C_6H_5COCH_2CH_2)_3N$ , hydrochloride, m.p. 201°; the latter is formed when acetophenone is heated with ammonium chloride and

formaldehyde. The base, when distilled with steam, breaks up with the formation of *phenyl-vinyl ketone* (p. 460) (*Schäfe*, Ber. 39, 2181).

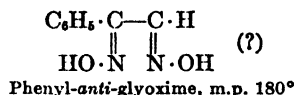
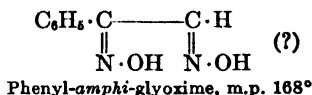
#### 4. Phenyl-aldehyde Ketones

**$\alpha$ -KETOALDEHYDES.** Phenyl-glyoxal,  $C_6H_5CO \cdot CH(OH)_2$ , m.p.  $73^\circ$ , b.p. of the anhydrous substance  $108-110^\circ$  (15 mm.), has a pungent smell. It can be prepared from its aldoxime, isonitroso-acetophenone, by boiling the bisulphite compound of the latter with dilute sulphuric acid (*Müller*, Ber. 22, 2557), or with crystals of nitroso-yl-sulphuric acid (*Neuberg*, Bio. Z. 229, 443), or in 60% yield, by oxidising a neutral aqueous solution of benzoyl carbinol with copper acetate (*Henze*, Physiol. Ch. 198, 102); or by brominating benzoyl-carbinol acetate, and acting on the product with sodium hydroxide (*Madelung*, Ber. 65, 935). Alkalis convert it into mandelic acid (p. 409). Under the influence of KCN it condenses to benzoyl-formoin, just as benzaldehyde condenses to benzoin. With diamines it forms quinoxalines (Vol. IV); with dimethylaniline it gives benzoyl-tetramethyl-diamino-diphenyl-methane (*Madelung*, loc. cit.). Its *aldehydo-hydrazone*,  $C_6H_5CO \cdot CH:N \cdot NH_2$ , m.p.  $120-121^\circ$ , is obtained by the action of hydrogen sulphide on diazo-acetophenone (*Wolff*, Ann. 394, 23).

$\omega$ -Dichloroacetophenone,  $C_6H_5COCHCl_2$ , b.p.  $253^\circ$  (*Dyckerhoff*, Ber. 10, 531).  $\omega$ -Dibromoacetophenone,  $C_6H_5COCHBr_2$ , m.p.  $36^\circ$  (*Hunnins*, Ber. 10, 2010; *Fittig*, Ann. 195, 167; *Evans*, Am. 35, 1770). Diiodoacetophenone, see p. 405.  $\omega$ -Dichloro-*o*-nitroacetophenone, m.p.  $73^\circ$  (*Gevekoht*, Ann. 221, 328).  $\omega$ -Dichloro-*o*-nitroacetophenone, m.p.  $73^\circ$  (*Gevekoht*, Ann. 221, 328).  $\omega$ -Dibromo-*o*-, *m*-, and *p*-nitroacetophenone, m.p.  $85^\circ$ ,  $59^\circ$ ,  $98^\circ$ , respectively (*Engler*, Ber. 18, 2240; 20, 2220; 22, 204). Benzoylmethionol,  $C_6H_5CO \cdot CH(SO_2C_2H_5)_2$ , m.p.  $96^\circ$ , is obtained by heating diphenyl methionate and benzoyl chloride in benzene solution with sodium (*Schroeter*, Ann. 418, 235). *m*-Nitrobenzoyl-formaldehyde,  $(O_2N)[3]C_6H_4CO \cdot CHO$ , is a viscous, straw-coloured oil, obtained from the carbinol by heating it with aqueous cupric acetate (*Evans*, Am. 33, 1772).

Isonitroso-acetophenone, benzoyl-formoxime,  $C_6H_5CO \cdot CH(N \cdot OH)$ , m.p.  $127^\circ$ , is prepared from acetophenone (p. 283) (*Soderbaum*, Ber. 25, 3459; *Wieland*, Ann. 358, 56). When reduced it gives diphenyl-pyrazine (Vol. IV).

Phenyl-glyoxime,  $C_6H_5 \cdot C(NO_2) \cdot CH(NO_2)$ , is known in two modifications (cf. benzil-dioximes):



Phenyl-amphiglyoxime is prepared from  $\omega$ -dibromoacetophenone or isonitroso-acetophenone by the action of hydroxylamine. With hydrogen chloride in pure ether it changes into the *anti*-form, but this reverts to the *amphi*-form on recrystallisation from an indifferent solvent; cf. phenyl-glyoxime peroxide and phenyl-furoxan (*Russanov*, Ber. 24, 3497). *p*-Tolyl-glyoxime and *p*-chloro- and *p*-bromo-phenyl-glyoximes also exist in two forms; they are prepared in a similar way to phenyl-glyoxime from the  $\omega$ -dibromo derivatives of the corresponding acetophenones (*Avogadro*, Gazz. 53, 689). *Ponzo* has published many papers on the chemistry of the glyoximes in Gazz. chim. ital.

Phenylglyoxal- $\alpha$ -phenylhydrazone,  $C_6H_5C(NNHC_6H_5)CHO$  (?), is known in two forms:  $\alpha$ -form, m.p.  $134-135^\circ$ , and  $\beta$ -form, m.p.  $145-146^\circ$  (*Sidgwick*, J. 119, 486); it is obtained by the action of phenylhydrazine on phenyl-glyoxal. The  $\beta$ -hydrazone,  $C_6H_5COCH:NNHC_6H_5$ , exists in two modifications, which are easily converted into each other, m.p.  $138^\circ$  and  $114^\circ$ . It is obtained by the action of diazo-benzene on benzoyl-acetic acid (*Bamberger*, Ber. 34, 2001; *Müller*, Ber. 22, 2557).

Phenylglyoxal-phenylosazone,  $C_6H_5 \cdot C:(N \cdot NHC_6H_5) \cdot CH:(N \cdot NHC_6H_5)$ , m.p.  $152^\circ$ , is obtained from benzoyl carbinol (*Müller*, loc. cit.). Phenylglyoxal-methylphenylosazone, m.p.  $152^\circ$  (*Culman*, Ber. 21, 2597).

*p*-Toluyal-formaldehyde,  $CH_3C_6H_4CO \cdot CH(OH)_2$ , m.p.  $101^\circ$  (*Müller*, loc. cit.).

Anthroxan-aldehyde,  $C_6H_5 \cdot C \begin{array}{c} \diagup \quad \diagdown \\ O \quad N \end{array} CHO$ , m.p.  $72^\circ$ , is obtained from *o*-nitrophenyl-glycidic acid (*Schillinger*, Ber. 16, 2222) (p. 421; cf. anthranil, p. 278).



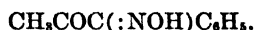
**$\beta$ -Ketoaldehydes.** A compound called *formyl-acetophenone* or *benzoyl-acetaldehyde*, was formerly considered to be a  $\beta$ -ketoaldehyde, but, like formyl-acetone (p. 484), it is an unsaturated ketol, hydroxymethylene-acetophenone, and will be dealt with among the compounds with unsaturated side-chains. The sodium-compound of this hydroxymethylene-acetophenone gives **benzoyl-acetaldoxime**,  $C_6H_5 \cdot CO \cdot CH_2 \cdot CH : NOH$ , m.p.  $98^\circ$ , with hydroxylamine hydrochloride; and with acetic anhydride it gives cyanoacetophenone (p. 430). With acetyl chloride it gives 5-phenyl-isoxazole (Vol. IV). **Aceto-phenylacetaldehyde**, *hydroxymethylene-benzyl-methyl-ketone*,  $CH_3CO \cdot CH(C_6H_5)CHO$  or  $CH_3CO \cdot C(C_6H_5) : CHO$ , m.p.  $67-69^\circ$ , is very unstable. It is formed by the rearrangement of benzylidene-acetone oxide (p. 459), a change that is brought about by boiling with hydrochloric acid. It dissolves in caustic soda, gives a copper salt, and a phenylhydrazone, m.p.  $171^\circ$  (Weitz, Ber. 54, 2344).

**$\gamma$ -Ketoaldehydes.** **Benzoyl-propionaldehyde**,  $C_6H_5CO \cdot CH_2CH_2CHO$ , b.p.  $245^\circ$ .

## 5. Phenyl Paraffin Diketones

**$\alpha$ -Diketones**, or *ortho-diketones*, are formed when their monoximes, the phenyl-isonitroso-ketones (see above, phenyl glyoxal), are distilled with dilute acids, or heated with amyl nitrite (Pechmann, 1888; Menasse, Ber. 21, 2146). For the keto- and enol-forms, see Lowry, J. 1928, 3167.

**Acetyl-benzoyl**,  $C_6H_5 \cdot CO \cdot CO \cdot CH_3$ , b.p.  $214^\circ$ , is a yellow oil with a pungent odour. It is formed by the above methods, and also by the oxidation of the two stereoisomeric phenyl-methyl-glycols (p. 398) with nitric acid (Zincke, Ber. 43, 855). It is a by-product in the biochemical synthesis of 1-phenyl-acetyl-carbinol (p. 406) (Neuberg, Bio. Z. 128, 610). For its conversion into ephedrine, see p. 402. **Acetylbenzoyl- $\alpha$ -aceto-hydrazone**,  $CH_3CO \cdot C(NNHCOCH_3)C_6H_5$ , m.p.  $154^\circ$ , dissolves in sodium hydroxide giving a salt of the pseudo-form (Diels, Ber. 36, 3187).  **$\alpha$ -Hydroximido-propio-phenone**,  $C_6H_5CO \cdot C : (NOH) \cdot CH_3$ , m.p.  $113^\circ$ , can be obtained by the action of nitrous acid on methyl-benzoyl-acetic ester, by the action of butyl nitrite on propiophenone (Hartung, J. 1928, 3167) or by the action of phenyl-diazonium chloride on an alkaline solution of isonitroso-acetone, in which reaction it is probable that a phenyl-azo-aldoxime is an intermediate product (Borsche, Ber. 40, 747).



**Phenyl-isonitrosoacetone**,  $C_6H_5C : (NOH)COCH_3$ , m.p.  $165^\circ$ , is formed by the action of amyl nitrite on phenyl-acetone in the presence of sodium ethoxide. **Phenyl-methyl-glyoxime**,  $C_6H_5C : (NOH)C : (NOH)CH_3$ , m.p.  $239^\circ$  (Kolb, Ann. 291, 289), is obtained from phenyl-isonitrosoacetone, and *p*-methoxyphenyl-methyl-glyoxime,  $CH_3O[4]C_6H_4[C(NO)]_2CH_3$ , m.p.  $206^\circ$  (decomp.), is obtained from anethole by the action of nitrous acid. Its peroxide, m.p.  $97^\circ$ , is obtained at the same time (Wieland, Ann. 329, 268).

**$\beta$ -Diketones** or *meta-diketones* are formed, together with acetophenone: (1) by decomposing benzoyl-aceto-acetic esters (Fischer, 1883); (2) by condensing esters and ketones by means of sodium ethoxide (Claisen, Ber. 20, 2178) or in xylene with sodium (Lovett, J. 1928, 1975); (3) by decomposing the ethylene bases obtained from phenyl-acetenyl-alkyl ketones (p. 461) with acids (André, C.r. 152, 1488). Phenyl- $\beta$ -diketones behave like the aliphatic  $\beta$ -diketones. They dissolve in caustic alkalis, a fact which distinguishes them readily from other diketones. They give a red colouration with ferric chloride, and they condense with hydroxylamine to give *isoxazoles*, and with phenylhydrazine to give *pyrazoles* (Vol. IV). The keto- and enol-content of the diketones has been determined spectrochemically and by titration (Auwers, Ann. 426, 197).

**Benzoyl-acetone**, **acetyl-acetophenone**,  $C_6H_5CO \cdot CH_2COCH_3$ , m.p.  $60^\circ$ , b.p.  $261^\circ$ , is readily volatile with steam. It is obtained from benzoyl-acetoacetic ester, or from ethyl benzoate and acetone with sodium ethoxide free from alcohol, or from ethyl acetate and acetophenone, using the same condensing agent. It adds on hydrocyanic acid (Carlson, Ber. 27, 1571). For its reactions with urea

and guanidine see *Evans*, J. pr. 48, 489; for its alkylation, see *Dieckmann*, Ber. 45, 2685; for its reduction with sodium in dry alcohol see *Bauer*, C.r. 154, 1092. Its copper compound gives **thio-benzoyl-acetone**,  $S[CH(COCH_3)COC_6H_5]_2$ , m.p. 95°, with  $SCl_2$ , and **dithio-benzoyl-acetone**,  $S_2[CH(COCH_3)COC_6H_5]_2$ , m.p. 118°, with  $S_2Cl_2$  (*Vaillant*, Bull. [3], 29, 528). **p-Bromo-benzoyl-acetone**, m.p. 94–96° (decomp.), is obtained from *p*-bromo-acetophenone and ethyl acetate in ether, using sodium as condensing agent (*Hanus*, Trav. Tchecosl. 1, 392). **o-Nitro-benzoyl acetone**, m.p. 55° (*Gewekoht*, Ann. 221, 332). **Benzoyl-nitro-acetone** has been obtained, in the form of its oxime,  $C_6H_5C(NO_2) \cdot CH(NO_2)COCH_3$ , by the action of nitrogen trioxide on benzylidene-acetone (*Wieland*, Ber. 36, 3021).

**Propionyl, butyryl, isobutyryl, valeryl, and isovaleryl-acetophenone**, b.p.'s 172° (30 mm.), 174° (24 mm.), 170° (26 mm.), 183° (30 mm.), and 160–161° (11 mm.), respectively (*Baeyer*, Ber. 20, 2181; *Auwers*, Ann. 426, 161).

**Phenyl-acetyl-acetone**,  $C_6H_5 \cdot CH_2COCH_2COCH_3$ , b.p. 266°, is obtained by the decomposition of phenyl-acetyl-acetoacetic ester (*Fischer*, Ber. 18, 2136).

**$\gamma$ -Diketones.** **Acetophenone-acetone**, **phenacyl-acetone**,  $C_6H_5COCH_2CH_2COCH_3$ , is a yellow oil, which decomposes on boiling and is obtained by the decomposition of acetophenone-acetoacetic ester (p. 434) (*Paal*, Ber. 17, 2756). Being a  $\gamma$ -diketone (Vol. I, p. 404) it is easily converted into phenyl-methyl-furfuran, -thiophene or -pyrrole.

**Triketones.** **Phenyl-methyl-triketone**, b.p. 138° (24 mm.), is an orange-coloured oil, which readily takes up water to form a colourless hydrate, m.p. 54–58°, and forms addition compounds with acetyl-acetone and similar compounds. It reduces cupric salts. Its **dimethyl-amino-anil**,  $C_6H_5COC[NC_6H_4N(CH_3)_2]_2COCH_3$ , m.p. 99°, is obtained from benzoyl-acetone and nitroso-*d* dimethylaniline, and gives the free triketone on dissociation. Benzoyl-acetone reacts with diazo-salts to give **phenyl-azobenzoyl-acetone**,  $C_6H_5COCH \cdot (N_2C_6H_5)COCH_3$ , m.p. 99°, and with nitrous acid it gives **isomnitroso-benzoyl-acetone**,  $C_6H_5COC(NO_2)COCH_3$ , m.p. 125°. This is reduced to benzoyl-amino-acetone with zinc and sulphuric acid, and this compound gives **diazo-benzoyl-acetone**, m.p. 66°, with nitrous acid. This diazo-diketone (Vol. IV) is decomposed by ammonia into acetic acid and diazo-acetophenone (p. 405), and by boiling water into nitrogen, carbon dioxide, and benzyl-methyl-ketone,  $C_6H_5CH_2COCH_3$ , a rearrangement having taken place. For other reactions, see the heterocyclic compounds, 1,2,3-oxadiazoles (Vol. IV) (*Wolff*, Ann. 325, 136).

**Phenacyl-diacetyl-methane**,  $C_6H_5COCH_2CH(COCH_3)_2$ , m.p. 58°, is obtained from phenacyl bromide and sodio-acetyl-acetone. It is a 1,3- and a 1,4-diketone at one and the same time; hence it gives isoxazoles and pyrazoles, as well as *furo*-furans and pyrroles (*March*, C.r. 134, 843).

**Tetraketones:** **Benzylidene-bis-acetyl-acetone**,  $C_6H_5CH[CH(COCH_3)_2]_2$ , is formed by the condensation of benzaldehyde and acetyl-acetone in the presence of piperidine. Six allotropic keto- and enol-forms in *cis*- and *trans*-modifications are possible, and all have been prepared.

## 6. Phenyl Paraffin Alcohol Acids

### (a) Monohydroxy-ulcohol Acids

Like the aliphatic alcohol-acids, phenyl-alcohol-carboxylic acids are formed: (1) by the reduction of keto-acids; (2) by adding HCN to aldehydes and ketones and hydrolysing the resulting  $\alpha$ -hydroxy-nitriles (*Gabriel*, Ber. 12, 815); (3) from monohalogeno-acids; and (4) from unsaturated monocarboxylic acids, etc.

**$\alpha$ - and  $\beta$ -HYDROXY-ACIDS.** **Mandelic acid**, **phenyl-glycolic acid**,  $C_6H_5 \cdot CHOH \cdot COOH$ , is isomeric with the cresotic acids (p. 363), the hydroxymethyl-benzoic acids and the methoxy-benzoic acids (p. 375). It contains an asymmetric carbon atom, and like fermentation lactic acid (Vol. I, p. 415) it occurs in an inactive and two optically active modifications. The former can be resolved.

**Paramandelic acid** or *inactive mandelic acid*, m.p. 118°, is obtained: (1) from benzaldehyde, hydrocyanic acid, and hydrochloric acid; (2) by reduction of benzoyl-formic acid (p. 422) with sodium amalgam; (3) by boiling phenyl-chloroacetic acid with alkali; and (4) by the action of alkali on  $\omega$ -dibromo-acetophenone or phenyl-glyoxal:  $\text{C}_6\text{H}_5\text{CO}\cdot\text{CHO} \rightarrow \text{C}_6\text{H}_5\text{CHOH}\cdot\text{COOH}$  (*Spiegel, Tiemann, 1881*).

The formation of mandelic acid from phenyl-glyoxal is an intramolecular reaction which is essentially analogous to the extramolecular reaction which occurs when benzaldehyde gives an alcohol and a carboxylic acid under the action of alkali (p. 269). For the formation of paramandelic acid from *l*- and *d*-mandelic acids see below.

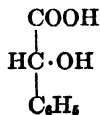
100 parts of water at 20° dissolve 15.9 parts of paramandelic acid. Dilute nitric acid oxidises it first to benzoyl-formic acid and then to benzoic acid. When heated with hydrogen iodide it is converted into phenyl-acetic acid (p. 293), and with hydrochloric or hydrobromic acids into phenyl-chloro- or phenyl-bromo-acetic acid, respectively. For its reaction with sulphuric acid, see *Oechsner, C.r. 136, 1469*.

*l*- and *d*-Mandelic acids both melt at 133°. They possess equal and opposite rotatory powers,  $[\alpha]_{\text{D}}^{20} = 153^\circ$  in 4% aqueous solution. Their reactions are the same as those of paramandelic acid. The natural mandelic acid formed from amygdalin is laevo-rotatory.

When ammonium paramandelate is fermented by *Penicillium glaucum*, the *l*-mandelic acid is consumed and the *d*-acid is left. Bacteria, on the other hand, destroy the *d*-acid first and leave the *l*-acid behind (*Levkovitch, 1884*). The direct resolution of paramandelic into the *d*- and *l*-mandelic acids can be accomplished by means of the cinchonine salt, or by means of *l*-phenyl-ethylamine (*Smith, J. pr. 84, 743; Marckwald, Ber. 34, 469*). Inactive mandelic acid is formed when equimolecular amounts of *d*- and *l*-mandelic acids are mixed, or when either is heated in a sealed tube at 160°. For the catalytic racemisation of ethyl-*l*-mandelate by alcoholysis, see *McKenzie, J. 115, 602*. Like some aliphatic  $\alpha$ -hydroxy-acids, mandelic acid can be acetonised with acetone and mineral acids. When mandelic amide is treated in this way, the ring closes, and a tetrahydro-

$\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}$   
 $\text{oxazalone, } \text{O} \text{---} \text{C}(\text{CH}_3)_2, \text{ m.p. } 127^\circ, \text{ is formed (Fischer, Ber. 60, 486; 65, 1032).}$

A direct interconversion of the two active forms is brought about as follows: *d*-mandelic acid, when acted upon by phosphorus pentachloride, gives *l*-phenyl-chloroacetic acid; this, when treated with ammonia, gives *d*-phenyl-glycocoll, and this with nitrous acid gives *l*-mandelic acid (Walden inversion, Vol. I, p. 70). In the same way, the conversion of *l*-mandelic acid into the *d*-form may be carried out. The configuration of *l*-mandelic acid is, according to *Freudenberg (Ber. 56, 193; Ann. 501, 199)*:



**Derivatives of paramandelic acid.** Methyl and ethyl esters, m.p. 52° and 34°, resp. (*Rupe, Ber. 28, 259*); amide, m.p. 131° (*Pulvermacher, Ber. 25, 2212*). The hydrazide, m.p. 132°, gives, with nitrous acid, a very unstable azide, which, unlike other azides of carboxylic acids, gives benzaldehyde, nitrogen, and allophanic ester when treated with alcohol (*Curtius, Ber. 34, 2794*). The methyl-ether acid, m.p. 71°, has been resolved:  $[\alpha]_{\text{D}} +168.2^\circ$  and  $-169.8^\circ$  (*Arch. Pharm. 270, 518*). Dimethyl-ether acid, b.p. 246° (*Meyer, Ann. 220, 40*). Diethyl-ether acid, see C. 1899, II, 622. Acetyl-mandelic acid, m.p. 80°; acetyl-mandelic chloride, b.p. 132° (12 mm.); amide, m.p. 112°; anilide, m.p. 117.5°; ethyl ester, m.p. 74° (*Wieland, Ann. 368, 57*). Mandelic chloralide, m.p. 82°

(Wallach, Ann. 193, 40). Diphenyl-glycolide,  $C_6H_5CH \begin{array}{c} \diagup O \cdot CO \\ \diagdown CO \cdot O \end{array} CHC_6H_5$ , m.p.

240°, is obtained by the action of carbonyl chloride on mandelic acid in pyridine (Einhorn, Ber. 35, 3642).

**Inactive mandelic nitrile**,  $C_6H_5CH(OH)CN$ , prisms, m.p. 22°, decomposes at 170° into hydrocyanic acid and benzaldehyde. Like mandelic acid, it exists in a dextro- and a laevo-rotatory form. When these are hydrolysed, active mandelic acids of opposite rotation are formed. When mandelic nitrile is allowed to stand with very concentrated hydrochloric acid, it gives the amide, but, at a higher temperature, phenyl-chloroacetic acid is formed (Tiemann, Ber. 14, 1967). On hydrogenation with pallidated carbon, the OH-group is reduced along with the CN group, and phenyl-ethylamine is formed (Hartung, Am. 50, 3370). It condenses with benzaldehyde in different ways: with dilute alcoholic hydrogen chloride, or with ethereal hydrocyanic acid it forms *di*-( $\alpha$ -cyano-benzyl-oxy)-phenyl-methane,  $C_6H_5CH(OCH(CN)C_6H_5)_2$ , m.p. 198°, which is also formed when mandelic nitrile is kept for some time (Baker, J. 1930, 1274). On the other hand, with ethereal hydrogen chloride, *diphenyl-oxazole* (Vol. IV) and *benzylidene-mandelic amide*,  $C_6H_5CH:NCOCH(OH)C_6H_5$ , are formed (Fischer, Ber. 29, 207; Stollé, Ber. 35, 1590). For glucosides of inactive and active mandelic nitriles see Vol. II, p. 365.

**Trichloromethyl- and tribromomethyl-phenyl-carbinols**,  $CCl_3CH(OH)C_6H_5$ , b.p. 155° (25 mm.), and  $CBR_3CH(OH)C_6H_5$ , m.p. 78°, are derivatives of mandelic acid obtained in a similar manner to acetone-chloroform (Vol. I, p. 418) by condensing chloroform or bromoform with benzaldehyde by means of caustic potash, or aluminium chloride; they can also be obtained from phenyl magnesium chloride or bromide and chloral; they can be converted into mandelic acid, and are reduced by zinc dust to styrene and halogeno-styrenes (p. 444). When boiled with potassium carbonate, they break down into benzaldehyde, and chloroform or bromoform (Savariau, C.r. 146, 297).

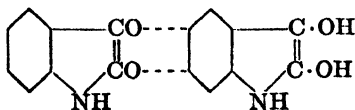
***p*-Dimethylamino-phenyl-trichloroethyl-alcohol**,  $(CH_3)_2NC_6H_4CH(OH)CCl_3$ , is obtained by the action of dimethylaniline on chloral (Boessneck, Ber. 19, 365). ***p*-Dimethylamino-mandelic nitrile**,  $(CH_3)_2N[4]C_6H_4CH(OH)CN$ , m.p. 114°, is obtained from *p*-dimethylamino-benzaldehyde (Sachs, Ber. 35, 3571).

***o*-, *m*-, and *p*-Chloro-mandelic acids**, m.p. 85°, 115°, 121°, obtained from the corresponding chloro-benzaldehydes by the action of potassium cyanide and hydrogen chloride in ether. Methyl esters, b.p. 134–136° (6 mm.), m.p. 84° and 55.6°, respectively. Amides, m.p. 87.5°, 126.5°, 125.5°, resp. (Jenkins, Am. 53, 2341). ***p*-Bromo-mandelic acid**, m.p. 117°; ***p*-iodo-mandelic acid**, m.p. 133° (Schweitzer, Ber. 24, 997).

***o*-, *m*-, and *p*-Nitro-mandelic acids**, m.p. 140°, 119°, and 126° (Engler, Ber. 20, 2203; 23, 208). ***o*-Nitro-mandelic nitrile** is reduced by zinc and hydrochloric acid to *o*-hydroxylamino-mandelamide, m.p. 140–141° (decomp.). When an aqueous solution of the hydrochloride of the latter is heated it gives *anthroxan-amide*, m.p. 211–212° (p. 426) (Reissert, Ber. 57, 964). For a peculiar reduction product of *o*-nitro-mandelic nitrile, and for the reduction of *p*-nitro-mandelic acid to *p*-azoxy- and *p*-amino-mandelic acids, see Heller, Ber. 41, 373; 46, 288.

***o*-Amino-mandelic acid**,  $NH_2[2]C_6H_4CH(OH)COOH$ , is unstable in the free state. Its sodium salt,  $C_6H_4NO_2Na + H_2O$ , is formed in the reduction of isatin with sodium amalgam. From the concentrated solution, acids precipitate.

**Dioxindole, 3-hydroxy-indole, *o*-amino-mandelic lactam**,  $C_6H_4 \begin{array}{c} \diagup [1]CH(OH)CO \\ \diagdown [2]NH \end{array}$ , m.p. 170° (indefinite). This compound is also formed when isatin is boiled with zinc dust and dilute HCl (Vol. IV). It is probable that *isatyde*, a substance with a quinhydrone structure:



is formed as an intermediate product (Heller, Ber. 62, 343). Dihydroxy-indole and isatin are degradation products of dehydro-indigo, under the action of mineral acids (Kalb, Ber. 44, 1455). Its  $\beta$ -derivatives have been prepared from isatin by the action of organo-magnesium compounds (Kohn, Mo. 32, 905). Acetyl-dihydroxy-indole, m.p. 127°, gives *o*-acetamino-mandelic acid,  $\text{CH}_3\text{CONH}[2]-\text{C}_6\text{H}_4\text{CH}(\text{OH})\text{COOH}$ , m.p. 142°, with baryta-water. This compound is also obtained by the reduction of acetyl-isatinic acid. It is converted into oxindole by hydriodic acid. With phenylhydrazine it gives isatin- $\beta$ -phenylhydrazone (Vol. IV) (Kenyon, J. 1931, 2275).

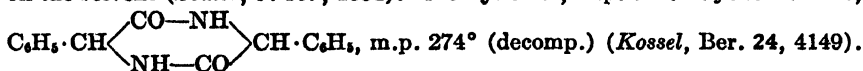
*o*-Hydroxy-mandelic acid is a syrupy mass, obtained by the action of hydrocyanic acid on salicylaldehyde and subsequent hydrolysis, and from *o*-hydroxy-phenyl-glyoxylic acid. By the action of hydrocyanic acid and subsequent hydrolysis on helicin tetra-acetate, an optically active hydroxy-mandelic acid is formed (Fischer, C. 1902, II, 214). *o*-Hydroxy-mandelic lactone, m.p. 49°, b.p. 237°. The nitrile of *o*-methoxy-mandelic acid, m.p. 71°, is formed from methyl-salicylaldehyde, or its bisulphite compound, by the action of potassium cyanide (Czaplicki, Ber. 42, 828). *p*-Methoxy-mandelic acid, m.p. 93°, is obtained from anisaldehyde, and 2,5-dihydroxy-mandelic acid, m.p. 143° (decomp.), is obtained by reduction of hydroquinone-glyoxylic acid (Neubauer, Physiol. Ch. 52, 375).

Phenyl-chloroacetic acid,  $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{COOH}$ , m.p. 78°, is obtained by heating mandelic acid to 140° with concentrated hydrochloric acid, or by the action of caustic potash on trichloromethyl-phenyl carbinol (see above), or by the action of water on its chloride; and the chloride,  $\text{C}_6\text{H}_5\text{CHCl}\cdot\text{COCl}$ , b.p. 125° (45 mm.), is obtained from mandelic acid by the action of phosphorus pentachloride. The optically active forms have been obtained from the racemic mixture by means of morphine (Darapsky, J. pr. 99, 179).

Phenyl-bromoacetic acid,  $\text{C}_6\text{H}_5\cdot\text{CHBr}\cdot\text{COOH}$ , m.p. 83°. Its ethyl ester, b.p. 145° (10 mm.), gives diphenyl-succinic ester when heated with potassium cyanide. Chloride, b.p. 118° (18 mm.). The nitrile, obtained by the action of bromine on benzyl cyanide, gives stilbene when heated alone, of dicyano-dibenzyl when heated with potassium cyanide, and stilbene-dicarboxylic, or diphenyl-maleic acid when heated with alcoholic potash.

Phenyl-nitroacetic ester and phenyl-nitroacetonitrile are obtained in the form of their sodium salts,  $\text{C}_6\text{H}_5\text{C}(\text{NOONa})\text{COOC}_2\text{H}_5$ , and  $\text{C}_6\text{H}_5\text{C}(\text{NOONa})\text{CN}$ , from phenyl-acetic ester and benzyl cyanide, respectively, by the action of ethyl nitrate and sodium ethoxide. The free acids are very unstable, and hydrolysis with sodium hydroxide gives phenyl sodio-phenyl-nitromethane (p. 256); when sodio-phenyl-nitroaceto-nitrile is reduced with zinc dust, isonitroso-benzyl cyanide,  $\text{C}_6\text{H}_5\text{C}(\text{NOH})\text{CN}$ , is formed (Wislicenus, Ber. 35, 1755; 42, 1930).

Phenyl-aminoacetic acid,  $\text{C}_6\text{H}_5\text{CH}(\text{NH}_2)\cdot\text{COOH}$ , m.p. 256°, breaks down on distillation into carbon dioxide and benzylamine. It is formed: (1) from phenyl-chloro- or -bromo-acetic acids by the action of aqueous ammonia; (2) from its nitrile by boiling with dilute sulphuric acid; (3) by reduction of the oxime or phenylhydrazone of benzoyl-formic acid. Its optically active forms,  $[\alpha]_D^{20} = 157.8^\circ$ , have been prepared by means of *d*-camphor sulphonic acid, or from the formyl compound, m.p. 180°, by means of cinchonine or quinine. The *l*-acid can also be isolated by subjecting the racemic acid to partial fermentation with yeast (Fischer, Ber. 41, 1296; Betti, *ibid.*, 2071). When phenyl-aminoacetic acid is prepared from active phenyl-chloroacetic acid, the sign of the rotation depends on the solvent (Seuter, J. 109, 1091). Methyl ester, m.p. 32°. Cyclic diamide,



The nitrile, a yellow oil, which crystallises slowly, is very unstable, and is formed by the action of ammonia on mandelonitrile.

*p*-Hydroxyphenyl-aminoacetic acid,  $\text{HO}[4]\text{C}_6\text{H}_4\text{CH}(\text{NH}_2)\text{COOH}$ , m.p. 240-245°, is a lower homologue of tyrosine (p. 415), and is prepared from anisaldehyde, potassium cyanide, and ammonium chloride; the resulting amino-cyanhydrin is hydrolysed, and the acid demethylated (Aloy, J. pharm. chim. 73, 481).

By the action of methylamine, hydrazine, aniline, and similar bases on phenyl-halogenoacetic acids, alkylated and phenylated phenyl aminoacetic acids have

been obtained (*Darapsky*, J. pr. 99, 179). Starting with phenyl-bromoacetic chloride, a number of di- and polypeptides, such as phenyl-glycyl-glycine, phenyl-glycyl-alanine, etc., have been prepared (*Schmüllin*, Ann. 340, 190).

$\alpha$ -Hydrazino-phenylacetic acid,  $C_6H_5CH(NH \cdot NH_2)COOH$ , m.p. 190°, is obtained from the diammonium salt of phenyl-glyoxylic hydrazone, by reduction with sodium amalgam, shaking with benzaldehyde, and decomposing the resulting benzyl-hydrazino-phenylacetic acid, m.p. 150° (*Darapsky*, J. pr. 96, 251). For other  $\alpha$ -hydrazino-phenyl-fatty acids, see *ibid*.

$\alpha$ -Anilino-phenyl-acetonitrile,  $C_6H_5CH(NHC_6H_5)CN$ , m.p. 85°, is readily obtained by the action of hydrocyanic acid on benzylidene-aniline (p. 273), or by the action of aniline on mandelonitrile. It combines with benzaldehyde on boiling with alcoholic potash, a benzylidene compound of the corresponding acid amide being formed:



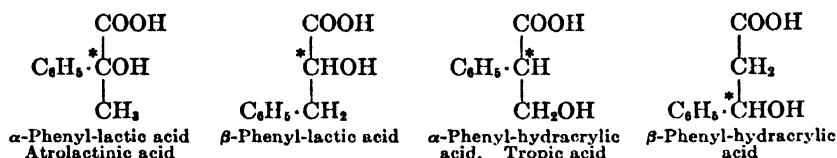
This very stable compound is also obtained by the action of potassium cyanide on a mixture of benzylidene-aniline and benzaldehyde (*Miller*, Ber. 31, 2699). *p*-Dimethylamino-phenyl-anilido-acetonitrile,  $(CH_3)_2NC_6H_4CH(NHC_6H_5)CN$ , m.p. 114° (*Sachs*, Ber. 35, 3572).

Urethano-phenyl-acetonitrile,  $C_6H_5CH(NHCOOC_2H_5)CN$ , m.p. 83°, is obtained from mandelonitrile by the action of urethane and zinc chloride (*Lehmann*, Ber. 34, 370).

Phenyl-sulphoacetic acid,  $C_6H_5CH(SO_3H)COOH + 2H_2O$ , m.p. about 140° (decomp.), is obtained by the action of ammonium sulphite on ammonium or ethyl phenylacetate, together with mandelic acid (*Brust*, Rec. 47, 153).

Of the aryl-glycolic acids, *p*-isopropyl-mandelic acid should be mentioned. It is prepared from cuminic aldehyde, hydrocyanic acid and hydrogen chloride. It has been resolved into its optical antipodes by means of quinine (*Fileti*, Gazz. 22, II, 395).

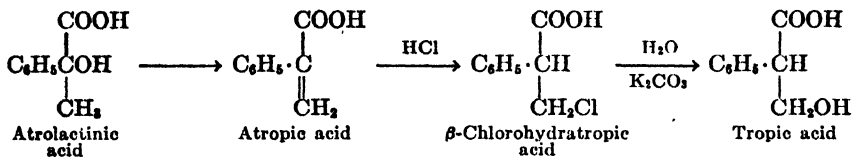
**PHENYL-HYDROXY-PROPIONIC ACIDS or PHENYL-LACTIC ACIDS.** Four structural isomers are possible, and all are known. They all contain an asymmetric carbon atom:



1. Atrolactinic acid,  $\alpha$ -phenyl-lactic acid,  $C_6H_{10}O_3 + \frac{1}{2}H_2O$ , m.p. of the hydrate 68°, and of the anhydrous substance, 94°. The acid is obtained from  $\alpha$ -bromo-hydratropic acid by boiling with aqueous sodium carbonate, by the action of permanganate on hydratropic acid, and from its nitrile, the addition product of hydrocyanic acid and acetophenone, by boiling with dilute HCl (*Tiemann*, Ber. 14, 1980; *Smith*, J. pr. 84, 731; *Freudenberg*, Ann. 501, 214). Its ethyl ester, b.p. 259°, can be obtained from phenyl-glyoxylic ester (p. 422) by the action of methyl magnesium iodide (*Grignard*, C.r. 135, 627). For its configurative relationship to mandelic acid, see *Freudenberg*, Ann. 501, 203. When boiled with concentrated hydrochloric acid, or distilled with water at reduced pressure, the acid breaks up into atropic acid and water. When heated at 140–160° in a current of carbon dioxide, it is converted into a mixture of  $\alpha$ - and  $\beta$ -isatropic acids (*Wren*, J. 113, 832). On standing with conc. HCl or NBr it is converted into  $\alpha$ -chloro- and  $\alpha$ -bromo-hydratropic acids, m.p. 73° and 93° (*Merling*, Ann. 209, 3).  $\alpha$ -Amino-hydratropic acid sublimes at 260° without melting (*Tiemann*, Ber. 14, 1981). For the resolution of racemic atrolactinic acid into its antipodes, see *Smith*, loc. cit., and *Wren*, J. 119, 798.

2. Tropic acid,  $\alpha$ -phenyl-hydracrylic acid, is known in one inactive form, which can be resolved, and in two optically active forms. Inactive tropic acid, m.p. 117°, is formed, together with tropine (Vol. IV) when the alkaloids atropine and

hyoscyamine are warmed at 60° with baryta water (*Lossen*, Ann. 138, 233; *Ladenberg*, Ber. 13, 254). It has been synthesised from atropic acid, the decomposition product of atrolactic acid, by treating it with concentrated hydrochloric acid, and thus converting it into  $\beta$ -chloro-hydrotropic acid, which gives inactive tropic acid on boiling with aqueous potassium carbonate. Another synthesis consists in reducing either of the two forms of the so-called formyl-phenyl-acetic ester (p. 422) with aluminium amalgam and water or damp ether (*Müller*, Ber. 51, 252; *Wislicenus*, *ibid.*, 1237; *Braun*, Ber. 53, 1409).

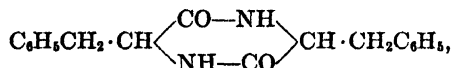


**Dextro- and laevo-tropic acids**, m.p. 128° and 128–129°, can be separated by the fractional crystallisation of their quinine salts, and are obtained in this way from *d,l*-tropic acid. The quinine salt of the *d*-acid, m.p. 186°, is less soluble in dilute alcohol than that of the *l*-acid, m.p. 189–190° (corr.).  $\beta$ -Chloro- and -bromo-hydrotropic acids, m.p. 87° and 93°.  $\beta$ -Amino-hydrotropic acid, m.p. 119° (*Merling*, Ann. 209, 3).

3.  $\beta$ -Phenyl-lactic acid,  $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{CH}(\text{OH})\text{COOH}$ , m.p. 97°, is obtained by the action of hydrocyanic and hydrochloric acids on phenyl-acetaldehyde, or by heating benzyl-tartronic acid (p. 436). When heated with dilute sulphuric acid it decomposes into phenyl-acetaldehyde and formic acid; for its resolution, see *Wren*, J. 119, 798.

$\alpha$ -Bromo-hydrocinnamic acid,  $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{CHBr}\cdot\text{COOH}$ , m.p. 49°, is obtained from benzyl-malonic acid by bromination and loss of carbon dioxide; chloride, b.p. 133° (12 mm.) (*Fischer*, Ber. 39, 3999).

**Phenylalanine**,  $\beta$ -phenyl- $\alpha$ -aminopropionic acid,  $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{CH}(\text{NH}_2)\text{COOH}$ , sublimes without decomposition when slowly heated, but on rapid heating it forms phenylethylamine, and a cyclic diamide,

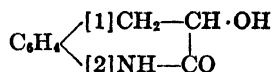


m.p. 290° (*Erlenmeyer*, Ann. 219, 188; 271, 169). Its laevo-form,  $[\alpha]_D^{20} = -35.1^\circ$ , occurs in germinating *Lupinus luteus*, together with asparagine (Vol. I, p. 609), and in beet shoots, together with *tryptophan* (Vol. IV) (*Lippmann*, Ber. 49, 106). It is formed when ovalbumin, casein, or glue are allowed to putrefy, or are decomposed chemically. It is isolated from mixtures by means of its sparingly soluble phosphotungstic compound (*Schulze*, Physiol. 35, 210). The nitrile of the inactive form is synthesised by treating  $\beta$ -phenyl-lactic nitrile with ammonia, followed by hydrochloric acid. Other methods of synthesis are: from benzyl-malonic azide by heating its aqueous solution (*Curtius*, Ber. 55, 1543); from benzyl-aceto-acetic ester by the action of hydrazoic acid in the presence of mineral acids (*Schmidt*, Ber. 57, 704; U. S. Pat. 1,564,631); reduction of  $\alpha$ -amino-cinnamic acid (*Plochl*, Ber. 17, 1623), or of  $\alpha$ -isonitroso- $\beta$ -phenylpropionic acid (*Erlenmeyer*, Ann. 271, 169); decomposition of phthalimino-benzyl-malonic ester,  $\text{C}_6\text{H}_4(\text{CO})_2\text{NC}(\text{CH}_2\text{C}_6\text{H}_5)(\text{COOR})_2$  (*Sørensen*, C. 1903, II, 33); and the action of ammonia on  $\alpha$ -bromo-hydrocinnamic acid. For the preparation of phenyl-alanine from *N*-benzyl-sulphonyldantoin, by condensing it with benzaldehyde, removing the benzoyl group and reducing with tin and hydrochloric acid, see *Johnson*, J. Biol. Chem. 12, 205. From the inactive phenylalanine thus obtained, the *d*- and *l*-forms  $[\alpha]_D^{20} = \pm 35^\circ$ , can be prepared by resolving the formyl compound by means of brucine, and also by partial fermentation with yeast (*Fischer*, Ann. 357, 2; *Ehrlich*, Bioch. Z. 8, 434). ***N*-Benzyl-phenylalanine**, m.p. about 225° (decomp.), is obtained from *d*,  $\alpha$ -bromohydrocinnamic acid and benzylamine (*Fischer*, Ber. 49, 1360). **Benzoyl-phenylalanine**, m.p. 182°, is formed by the reduction of benzoyl-amino-cinnamic acid, and **phenacetyl-phenyl-**

**alanine**,  $C_6H_5CH_2CH(NHCOCH_3C_6H_5)COOH$ , m.p.  $126^\circ$ , can be obtained similarly, but is also formed in a peculiar reaction by the action of ammonia on phenyl-pyruvic acid (p. 428) (*Erlenmeyer*, *Ann.* 275, 15; 307, 146). **Ethyl-phenyl-alaninate**, b.p.  $143^\circ$  (10 mm.) (*Fischer*, *Ber.* 34, 433).

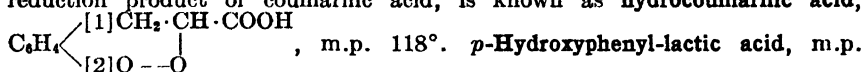
A great number of di- and polypeptides containing the phenylalanine complex have been prepared, such as phenylalanyl-glycine, phenylalanyl-phenylalanine, leucylglycyl-phenylalanine, etc. The methods used have been described in Vol. I, p. 445, and active and inactive phenylalanine, as well as  $\alpha$ -bromo-hydrocin-namic chloride, have been used as starting materials (*Fischer*, *Ann.* 354, 1; *ibid.*, 357, 1).

*o*- and *p*-Nitrophenyl-lactic acid are formed when phenyl-lactic acid is nitrated. On reduction, the *o*-acid gives *hydroxy-hydro-carbostyryl* (p. 418):



m.p.  $197^\circ$ , and the *p*-acid gives *p*-aminophenyl-lactic acid,  $NH_2[4]C_6H_4CH_2-CH(OH)COOH$ , m.p.  $188^\circ$  (decomp.).

*o*-Hydroxyphenyl-lactic acid,  $HO[2]C_6H_4CH_2CH(OH)COOH$ , is a syrup. It is obtained by the action of sodium amalgam on *o*-hydroxyphenyl-pyruvic acid (p. 428) (*Plochl*, *Ber.* 18, 1188). Its internal phenyl-alcohol anhydride, the reduction product of coumarilic acid, is known as **hydrocoumarilic acid**,



is obtained by the action of excess nitrous acid on *p*-amino-phenylalanine (*Fittig*, *Ann.* 216, 166; *Erlenmeyer*, *Ann.* 219, 226). **2,4-Dihydroxy-phenyl-lactic acid**, m.p.  $87^\circ$  (*Neubauer*, *Physiol.* 52, 375). ***p*-Iodophenylalanine**, m.p.  $270^\circ$  (decomp.) (*Wheeler*, *Am. Chem. J.* 40, 458; *Abderhalden*, *Ber.* 42, 3411). ***p*-Nitro-phenylalanine**,  $NO_2[4]C_6H_4CH \cdot CH(NH_2) \cdot COOH$ , decomposes at  $240^\circ$ . It is obtained by nitrating phenylalanine. ***p*-Amino-phenylalanine**,  $NH_2[4]C_6H_4CH_2 \cdot CH(NH_2)COOH$ , is the reduction product of *p*-nitro-phenylalanine and of *p*-nitrophenyl- $\alpha$ -nitroacrylic acid.

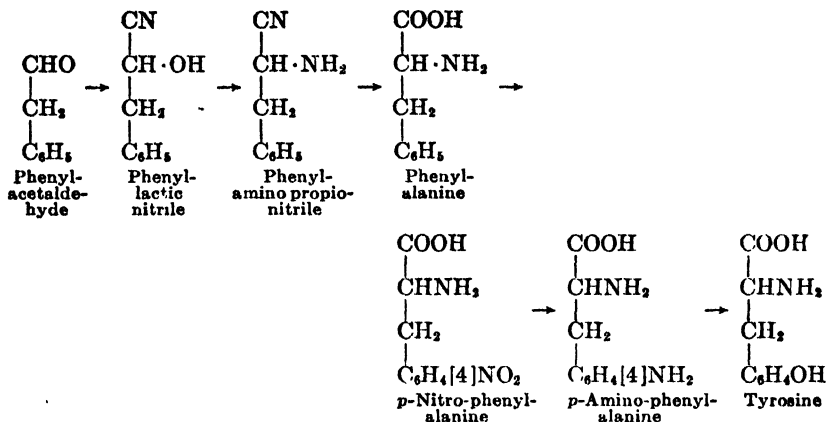
*o*-Hydroxy-phenylalanine, *o*-tyrosine,  $HO[2]C_6H_4CH_2CH(NH_2)COOH$ , m.p.  $232-233^\circ$  and  $270^\circ$ , is prepared by condensing thiohydantoin with salicylaldehyde, desulphurising, reducing, and decomposing the condensation product (*Johnson*, *Am.* 37, 1846).

**Tyrosine**, *p*-hydroxy-phenylalanine,  $HO(4)C_6H_4CH_2CH(NH_2)COOH$ , m.p.  $314-318^\circ$  (decomp.),  $[\alpha]_D -9.5$  to  $-10^\circ$ , occurs in the liver in cases of disease, in the spleen, in the pancreas, and in old cheese (*τυρός*). It is formed from many animal substances, such as urine, hair, and albumin, when they are boiled with hydrochloric or sulphuric acid, or fused with caustic potash, or together with leucine, asparagine, etc., on putrefaction. For its preparation, see *Rabaut*, *Bull.* 3, 391, and *Marshall*, *J. Biol. Ch.* 15, 85. It can be obtained synthetically by treating *p*-amino-phenylalanine with an equimolecular quantity of nitrous acid, or by decomposing synthetic benzoyl-tyrosine (see below).

**History.**—*Liebig* (1846) first obtained tyrosine by fusing fresh cheese with caustic potash (*Ann.* 57, 127; 62, 269). *E. Erlenmeyer, Sr.*, and *Lipp* (1883) succeeded in synthesising it from phenyl-acetaldehyde (*Ann.* 219, 161).

**Syntheses of tyrosine.**—(1) Phenyl-acetaldehyde, acted upon with hydrocyanic acid, gives phenyl-lactonitrile, and this with ammonia gives the nitrile of phenylalanine. The latter is converted into phenylalanine by hydrochloric acid. This is nitrated to *p*-nitrophenyl-alanine and then reduced to *p*-amino-phenylalanine hydrochloride. This gives tyrosine when treated with an equimolecular quantity of nitrous acid.





(2) A more convenient method has been discovered by *E. Erlenmeyer, Jr.*: *p*-hydroxy-benzaldehyde and hippuric acid condense under the action of sodium acetate and acetic anhydride to form an internal anhydride, a so-called azlactone, or oxazolone,  $\text{HOC}_6\text{H}_4\text{CH}:\text{C} \begin{array}{l} \text{N}=\text{C} \cdot \text{C}_6\text{H}_5 \\ \text{CO}-\text{O} \end{array}$ , of *p*-hydroxy- $\alpha$ -benzoyl-aminocinnamic acid,  $\text{HOC}_6\text{H}_4\text{CH}:\text{C}(\text{NHCOC}_6\text{H}_5)\text{COOH}$ .

When the oxazolone is reduced with sodium amalgam or hydrogen iodide and phosphorus, benzoyl-tyrosine,  $\text{HOC}_6\text{H}_4\text{CH}_2\text{CH}(\text{NHCOC}_6\text{H}_5)\text{COOH}$ , m.p.  $192^\circ$ , is formed. This substance is racemic and can be resolved into *d*- and *l*-benzoyl-tyrosine, m.p.  $162^\circ$ , by means of its brusine or cinchonine salt (cf. *Abderhalden*, *Physiol.* **131**, 277). The *l*-benzoyl-tyrosine, on decomposition with 10% hydrochloric acid, gives *l*-tyrosine, identical with the natural substance, while from *d*-benzoyl-tyrosine, *d*-tyrosine,  $[\alpha]_D +8.64^\circ$ , and from racemic benzoyl-tyrosine, a racemic tyrosine is obtained. The latter is identical with the product of the *p*-amino-phenylalanine synthesis just mentioned (*Erlenmeyer*, *Ann.* **307**, 138; *Fischer*, *Ber.* **32**, 3638).

(3) Racemic tyrosine has been obtained also from phthalimino-malonic ester and *p*-methoxy-benzyl bromide by decomposing the product first formed (*Stephan*, *J.* **105**, 1152). For the separation of *d*-tyrosine from the racemate by means of yeast, see *Ehrlich*, *Bioch. Z.* **182**, 245. For its degradation by bacteria, see *Taudji*, *Acta Kyoto*, **2**, 115; for the configuration of natural tyrosine, see *Goldschmidt*, *Ber.* **66**, 784.

**Properties and reactions of tyrosine.**—Tyrosine dissolves in 150 parts of boiling water, and crystallises in slender silky needles; it is very slightly soluble in alcohol, and insoluble in ether. When its aqueous solution is boiled with mercuric oxide, a yellow precipitate is formed, which turns dark red when boiled for a short time with highly diluted fuming nitric acid. This is a delicate test. As an amino-acid, tyrosine combines with both acids and bases to form salts. *l*-Tyrosine is converted by *Bacillus proteus* into *d*,*p*-hydroxyphenyl-lactic, or hydroxyphenylacetic, or hydroxyphenyl-acrylic acids, according to the conditions (*Hirai*, *Otsuka*, *Bioch. Z.* **114**, 71, 81; *Sasaki*, *J. Biol. Ch.* **32**, 533). The diazo-reaction of albumin is due to the presence of tyrosine in the complex (*Pauly*, *Physiol.* **94**, 284). When heated to  $230^\circ$ , tyrosine decomposes into carbon dioxide and hydroxyphenyl-ethylamine, or *tyramine*,  $\text{C}_6\text{H}_4(\text{OH})\text{CH}_2\text{CH}_2\text{NH}_2$  (p. 337). *l*-Tyrosine is racemised when warmed with sodium hydroxide (*Waser*, *Helv.* **6**, 199). When fused with caustic potash, tyrosine gives *p*-hydroxybenzoic acid, ammonia, and acetic acid. It gives hydro-*p*-coumaric acid (p. 365) on putrefaction, and *p*-hydroxyphenyl-lactic acid when treated with nitrous acid (*Erlenmeyer*, *Ann.* **219**, 226). By catalytic reduction it is converted into a mixture of hexahydro-tyrosine and hexahydro-phenylalanine (*Waser*, *Helv.* **7**, 740). With hydrogen peroxide and ferric chloride, it is converted into a substance known as *tyrosine black*, the sodium compound of which is soluble in water, and inhibits the clotting of blood (*Adler*, *C.* **1922**, I, 1117).

**Tyrosine anhydride**,  $(C_9H_7O_2N)_2$ , together with an amorphous isomer of similar m.p., is obtained by heating tyrosine with glycerol at 180–190°. It forms needles, m.p. 278–279° (*Graziani*, *Lincei* 25, 1, 509). **N-Methyl-tyrosine**, *surinamine*,  $HO[4]C_6H_4CH_2\cdot CH(NHCH_3)COOH$ , m.p. 280°, occurs in the bark of *Geoffroya surinamensis*. On heating it loses carbon dioxide, and *p*-hydroxyphenyl-ethyl-methylamine is formed (*Winterstein*, *Physiol.* 105, 20). For its synthesis, see *Friedmann*, *Bioch. Z.* 27, 491.

*Fischer* and *Abderhalden* have synthesised a large number of di- and polypeptides (*Ber.* 41, 2840, 2860) by combining active and inactive tyrosine with other amino-acids. They also succeeded in isolating peptides containing the tyrosine complex; by hydrolysing silk-fibroin they obtained a dipeptide, glycerol-tyrosine, and a tetrapeptide (?) consisting of 2 molecules of glycerol, one of *d*-alanine, and one of *l*-tyrosine (*Ber.* 40, 3544).

**3-Nitro-tyrosine**, m.p. 222–224° (decomp.), is obtained, together with a little 2-nitro-tyrosine, by the action of dilute nitric acid on tyrosine (*Johnson*, *Am.* 37, 1863). **3-Amino-tyrosine**, m.p. 287° (decomp.) (*Waser*, *Helv.* 4, 658). **2-Amino-tyrosine**, m.p. 265° (decomp.) (*Funk*, *J.* 99, 554).

The occurrence in nature of inactive 3,5-diiodo-tyrosine,  $OH[4]I_2[3,5]C_6H_3CH_2\cdot CH(NH_2)COOH$ , m.p. 200°, is of great interest. It was first isolated from the coral *Gorgonia Carolini*, and therefore is also called *iodo-gorgonic acid*. It occurs, together with thyroxin (see below), in the thyroid gland, where it acts in a contrary manner to thyroxin. It is therefore used as an antidote to super-activity of the thyroid gland (*Lacquer*, *Angew.* 47, 572). It has been synthesised by the iodination of tyrosine in alkaline solution (*Wheeler*, *Am. Chem. J.* 33, 365). For polypeptides of 3,5-diiodo-*l*-tyrosine, see *Abderhalden*, *Ber.* 41, 1237.

**3,5,3',5'-Tetraiodo-4'-hydroxyphenyl-tyrosine**, **thyroxin**, is the hormone of the thyroid gland, and is essential to life. It is fully dealt with in Vol. II, p. 582.

**3,4-Dihydroxy-phenylalanine**,  $(HO)_2[3,4]C_6H_3CH_2CH(NH_2)COOH$ , m.p. (active form) 285°, (*d,l*) 271–272° (decomp.), is possibly the parent substance of adrenaline (p. 402). Its *l*-form,  $[\alpha]_D -14.28^\circ$ , occurs in the husks of *Vicia faba*, in the bodies of some kinds of cockchafer, and in the basal cells of the epidermis. Its synthesis starts with the azlactone obtained from vanillin and hippuric acid, which by fission and reduction is converted first into *m*-methoxy-benzoyl-tyrosine and then into 3,4-dihydroxy-phenylalanine (*Harington*, *Bioch. J.* 22, 407; *Fromherz*, *Physiol.* 91, 194). It is obtained in a similar way from protocatechuic aldehyde carbonate (*Funk*, *J.* 99, 554); and from vanillin by the action of glycine anhydride, and removing the methoxy group (*Hirai*, *Bioch. Z.* 114, 67). The *l*-form can be obtained from tyrosine by nitrating, reducing, diazotising, and boiling with copper sulphate (*Waser*, *Helv.* 4, 657). Hydrochloride, m.p. (active form) 209°. The substance is converted into a dark-coloured dyestuff by the action of an oxidase found in the basal cells of the epidermis (*Feigl*, *Bioch. Z.* 79, 209).

**3-Methoxy-4-hydroxy-phenylalanine**, m.p. 255–256°, and **3,4-dimethoxy-phenylalanine**, m.p. 249–250°, are obtained by a similar method to tyrosine (see above) from vanillin and methyl-vanillin, or by condensation with thiohydantoin (*Johnson*, *Am.* 35, 1606). Similarly, **2,4,5-trimethoxy-phenylalanine**, m.p. 217°, is obtained from asarylaldehyde. For other polyhydroxy-phenylalanines, see *Schaaf*, *Helv.* 7, 357.

**4.  $\beta$ -Phenyl-hydracrylic acid**,  $C_6H_5\overset{*}{C}H(OH)CH_2COOH$ , m.p. 93°, is obtained: by boiling  $\beta$ -bromo-hydrocinnamic acid with water (*Fittig*, *Ann.* 195, 138); by the action of bromoacetic ester and zinc on benzaldehyde (*Andrijevsky*, *Russ.* 40, 1535); and by reduction of benzoyl-acetic ester or of  $\alpha$ -chloro- $\beta$ -phenyl-hydracrylic acid (an addition product of hypochlorous acid and cinnamic acid) with sodium amalgam. Like the aliphatic  $\beta$ -hydroxy-acids, phenyl-hydracrylic acid is decomposed when heated with dilute sulphuric acid to give water, cinnamic acid, and a little styrene. With concentrated hydrochloric acid it gives  $\beta$ -chloro-hydrocinnamic acid (see below). For its alkyl esters and ethers see *Schrauth*, *Ber.* 44, 1432.

$\alpha$ -Methyl- $\beta$ -phenyl-hydracrylic acid,  $C_6H_5CH(OH)CH(CH_3)COOH$ , m.p. 95°.  $\beta$ , $\beta$ -Methyl-phenyl-hydracrylic acid,  $C_6H_5CH_2C(OH)(CH_3)COOH$ , m.p. 50–53°; its ester is obtained from acetophenone, bromoacetic ester, and zinc (*Lindenbaum*, Ber. 50, 1270).  $\alpha$ -Dimethyl- $\beta$ , $p$ -tolyl-hydracrylic acid, m.p. 112°.  $\alpha$ -Isopropyl-phenyl-hydracrylic acid, m.p. 107° (*Zeltner*, C. 1902, I, 1293; *Schroeter*, Ber. 40, 1589; 41, 5).

*o*-, *m*- and *p*-Nitrophenyl-hydracrylic acids,  $NO_2C_6H_4CH(OH)CH_2COOH$ , m.p. 126°, 105° and 132°, are obtained from the three nitro- $\beta$ -bromo-hydrocinnamic acids (see below) by treatment with sodium carbonate; the reaction goes on in the cold, with the simultaneous formation of *o*-, *m*-, and *p*-nitrophenyl-hydracrylic lac-



tones,  $NO_2C_6H_4CH(O-CO)CH_2$ , m.p. 124°, 98°, and 92°, which are representatives of the otherwise little known class of  $\beta$ -lactones (p. 445) (*Prausnitz*, Ber. 17, 595; *Einhorn*, Ber. 17, 1659).

*o*-Nitrophenyl-hydracrylic acid is also formed from *o*-nitrophenyl-hydracrylic aldehyde (p. 403) on oxidation with silver oxide (*Baeyer*, Ber. 16, 2206). When heated with dilute sulphuric acid to 190° it is converted into *o*-nitro-cinnamic acid. Its lactone, on boiling with water, breaks down into carbon dioxide and *o*-nitrostyrene. When *o*-nitrophenyl-hydracrylic acid is reduced it gives  $\beta$ -hydroxy-hydrocarbostyryl (p. 330).

$\beta$ -Chloro-,  $\beta$ -bromo-, and  $\beta$ -iodo-hydrocinnamic acids,  $C_6H_5\cdot CHX\cdot CH_2COOH$ , m.p. 126°, 137°, and 120°, are obtained from cinnamic acid by adding on hydrogen halide to cinnamic acid in water or glacial acetic acid (*Anschutz*, Ber. 11, 1221), or from  $\beta$ -phenyl-hydracrylic acid by the method given above. When heated, or boiled with water, the free acids break down into the hydrogen halides and cinnamic acid. When neutralised with sodium carbonate they decompose, even in the cold, into hydrogen halides, carbon dioxide, and styrene,  $C_6H_5CH:CH_2$ .

*o*-, *m*-, and *p*-Nitro- $\beta$ -bromo-hydrocinnamic acids,  $NO_2C_6H_4CHBr\cdot CH_2COOH$ , are obtained by adding on HBr in glacial acetic acid to the three nitro-cinnamic acids (*Prausnitz*, Ber. 17, 596; *Basler*, *ibid.*, 1494) (cf. nitrophenyl-hydracrylic lactones, above).

$\beta$ -Hydroxylamino-hydrocinnamic acids,  $C_6H_5CH(NHOH)\cdot CH_2COOH$ , m.p. 166° (decomp.), is obtained by adding on free hydroxylamine to cinnamic acid. On oxidation with ammoniacal silver nitrate it is converted into  $\gamma$ -phenyl-isoxazolidone (Vol. IV), and by nitrous acid into *N*-hydroxy- $\gamma$ -phenyl-isoxazolidone. On reduction it gives  $\beta$ -amino-hydrocinnamic acid,  $C_6H_5CH(NH_2)\cdot CH_2COOH$ , m.p. 231°, which, with nitrous acid, gives  $\beta$ -phenyl-hydracrylic acid. Nuclear substituted  $\beta$ -amino-hydrocinnamic acids are also obtained from substituted ethyl cinnamates by the action of hydroxylamine (*Posner*, Ber. 38, 2316; 39, 3515; Ann. 389, 29).  $\beta$ -Phenyl- $\alpha$ -aminobutyric acid,  $C_6H_5CH_2\cdot CH_2CH(NH_2)COOH$ , m.p. 295°, is obtained by reducing the oxime of benzyl-pyruvic acid (*Knoop*, Ber. 39, 1478).

$\gamma$ - and  $\delta$ -HYDROXY-ACIDS. Phenyl derivatives of the higher  $\gamma$ -hydroxyacids are known, beginning with phenyl-hydroxy-butyric acid. They readily form lactones.

$\gamma$ -Phenyl- $\gamma$ -hydroxybutyric acid,  $C_6H_5\cdot CHOH\cdot CH_2\cdot CH_2COOH$ , m.p. 75°, slowly decomposes at a temperature as low as 70° into water and the lactone, m.p. 37°, b.p. 306° (*Pechmann*, Ber. 15, 880). It can be obtained from phenyl-bromo-butyric acid and from  $\beta$ -benzoyl-propionic acid (p. 431). Its lactone is formed when styryl-acetic acid or phenyl-paraconic acid is boiled with dilute sulphuric acid (*Erdmann*, Ann. 228, 178; *Lesser*, *ibid.*, 288, 1921; *Fittig*, Ber. 33,

3519). For the relationship of *m*-tolyl-butyrolactone,  $CH_3C_6H_4CHCH_2CH_2COO$ , to cannabinol, the poisonous resin from Indian hemp, *Cannabis indica* (Vol. II, p. 511) see Arch. Pharm. 272, 213.  $\gamma$ -Anisoxy- $\gamma$ -butyrolactone, m.p. 53–55°, is obtained by the catalytic reduction of the corresponding keto-butyric acid (p. 432).

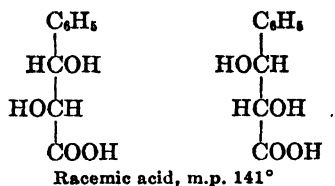
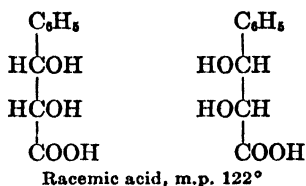
$\alpha$ -Phenyl- $\gamma$ -hydroxyvaleric acid is only stable as a liquid lactone (*Wellner*, Ber. 17, 73).  $\gamma$ -Phenyl- $\gamma$ -valerolactone, b.p. 169° (16 mm.), is obtained from laevulinic ester and phenylmagnesium bromide (*Grignard*, C.r. 135, 627).  $\delta$ -Phenyl- $\gamma$ -hydroxyvaleric acid, m.p. 101°; lactone, m.p. 33°.  $\beta$ -Benzyl- $\gamma$ -hydroxyvaleric

acid, m.p. 75°; lactone m.p. 85°, is obtained from benzylidene-laevulinic acid (Erdmann, Ann. 254, 215; Stern, *ibid.*, 268, 94; Weltner, Ber. 17, 73).  $\alpha$ -Benzyl- $\delta$ -hydroxyvaleric acid (Aschan, Ber. 24, 2447).

(b) Dihydroxy-alcohol Acids

These are usually prepared by oxidising phenyl-olefine-carboxylic acids with permanganate (Fittig, Ann. 268, 44; 283, 338). The two possible phenyl-glycerolic acids are known: Atroglycerolic acid,  $\alpha$ -phenyl-glycerolic acid,  $\text{CH}_2\text{OH} \cdot \text{C}(\text{C}_6\text{H}_5)(\text{OH}) \cdot \text{COOH}$ , m.p. 146°, is obtained by boiling  $\alpha, \beta$ -dibromohydratropic acid with excess of alkali, or by treating benzoyl carbinol (p. 403) with hydrocyanic acid and hydrochloric acid (Plöchl, Ber. 16, 1292). On heating it decomposes into carbon dioxide and phenyl-acetaldehyde. Dibromo-hydratropic acid,  $\text{CH}_2\text{Br} \cdot \text{CC}_6\text{H}_5\text{Br} \cdot \text{COOH}$ , m.p. 115°, is obtained by the action of bromine on atropic acid. When boiled with water it breaks down into acetophenone, carbon dioxide, and hydrobromic acid.

Styric acid,  $\beta$ -phenyl-glyceric acid,  $\text{C}_6\text{H}_5 \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COOH}$ , contains two asymmetric carbon atoms, and therefore occurs in a number of modifications. One of them, m.p. 122°, is obtained by hydrolysing the dibenzoyl ethyl ester,  $\text{C}_6\text{H}_5\text{CH}(\text{OCOC}_6\text{H}_5)\text{CH}(\text{OCOC}_6\text{H}_5)\text{COOC}_2\text{H}_5$ , m.p. 109°, with alcoholic potash. This ester is obtained by the action of silver benzoate on the dibromide of cinnamic ester. When it is hydrolysed by aqueous alkali, another acid, m.p. 141° (decomp.), is obtained, which is also formed when cinnamic acid is oxidised by permanganate in the cold. It is less soluble in ether than the first acid mentioned. Its ethyl ester, when carefully benzoylated, gives a dibenzoyl ester, m.p. 85°, while on benzoylation at a higher temperature a rearrangement takes place and the ester, m.p. 109°, is obtained. By the action of alkalis on phenyl- $\alpha$ -chlorohydracrylic acid, both acids are formed, phenyl-glycidic acid being an intermediate product. The acid, m.p. 122°, is racemic and can be resolved by means of its strychnine salt: *d*-form, m.p. 95°,  $[\alpha]_D$  in 7.64% acetone solution +27.49°; *l*-form, m.p. 97-98°,  $[\alpha]_D$  -25.6°. The acid of m.p. 141° has been resolved by means of its morphine ester into a *d*-form, m.p. 167°,  $[\alpha]_D$  +39.57°, and a *l*-form,  $[\alpha]_D$  -30.28°. The configuration of these two acids is arrived at from the fact that common fumaroid cinnamic acid gives, on oxidation with permanganate, the acid that melts at 141°, while maleinoid allocinnamic acid (p. 465) gives the acid m.p. 122° (cf. Vol. I, p. 710, tartaric acids) (Rieber, Ber. 41, 2411; 48, 823; 50, 893). Hence the two pairs of acids have the configurations:



When heated above their melting points these acids decompose into carbon dioxide and phenyl-acetaldehyde. When they are heated with sulphuric acid, concentrated hydrochloric acid, or acetic anhydride, they lose water and phenylpyruvic acid is formed (Dieckmann, Ber. 43, 1032). With hydrobromic acid, the acid of m.p. 122° gives a phenyl- $\beta$ -bromo- $\alpha$ -hydroxy-propionic acid, m.p. 157°, and the acid of m.p. 141° gives a bromo-hydroxy-acid of m.p. 165°.

Ethyl benzylidene-phenyl-glycerate,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{O} \cdot \text{CH}(\text{C}_6\text{H}_5) \cdot \text{O}) \cdot \text{CH} \cdot \text{COOC}_2\text{H}_5$ , is obtained in two stereoisomeric forms, m.p. 104° and 61°, by the action of diazoacetic ester on benzaldehyde. On hydrolysis, benzylidene-phenyl-glyceric acids, m.p. 132° and 156°, are formed. They are decomposed by acetic acid into benzaldehyde and the phenyl-glyceric acids of m.p. 122° and 141°. The benzylidene-phenyl-glyceric acid of m.p. 156° is reformed from the 141° acid by shaking it with benzaldehyde and 50% sulphuric acid (Dieckmann, Ber. 43, 1024).

*p*-Nitrophenyl-glyceric acid, m.p. 167°, is obtained from *p*-nitrophenyl-glycidic acid. *o*-Aminophenyl-glyceric acid, m.p. 218°.

$\beta$ -Phenyl- $\alpha$ -chloro-hydracrylic acid,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CHCl}\cdot\text{COOH} + \text{H}_2\text{O}$ , m.p. 56–57°, anhydrous 102–103°, is prepared by the action of hypochlorous acid on cinnamic acid (Rassow, J. pr. 84, 473). It is converted by sodium amalgam into phenyl-hydracrylic acid, and by alkalis into phenyl-glycidic acid, or phenyl-acetaldehyde, and phenyl-glyceric acid. Fuming hydrochloric acid gives phenyl-dichloro-propionic acid (Zimmer, Ber. 22, 3140).

$\beta$ -Phenyl- $\alpha$ -bromo-hydracrylic acid,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\cdot\text{CHBr}\cdot\text{COOH} + \text{H}_2\text{O}$ , exists in the anhydrous state in two high-melting racemic forms, the stable  $\alpha$ -modification, m.p. 125°, and the unstable  $\beta$ -modification, m.p. 126.5°; an optically active form, m.p. 119°, a low-melting racemic form, m.p. 69°, and an optically active form, m.p. 97°. It is obtained by boiling phenyl-dibromo-propionic acid with water (Bernier, Ber. 54, 1945). For the crystallographic constants of these forms, see Bernier, Z. Kryst. 56, 489. The m.p. and configurations of the  $\beta$ -phenyl- $\alpha$ -bromo- $\beta$ -hydroxy- and - $\beta$ -bromo- $\alpha$ -hydroxy-propionic acids are also given.

$\beta$ -Phenyl- $\alpha$ -iodo-hydracrylic acid,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\cdot\text{CHI}\cdot\text{COOH}$ , m.p. 137° (decomp.), is obtained by the action of iodine chloride on cinnamic acid (Erlenmeyer, Ber. 19, 2464). *o*- and *p*-Nitrophenyl- $\alpha$ -chloro-hydracrylic acids, m.p. 119° and 165°. The *o*-compound gives indole with sodium amalgam (Baeyer, Ber. 13, 2261; Lipp, Ber. 19, 2646).

$\beta$ -Phenyl- $\alpha$ -amino-hydracrylic acid, phenyl-serine,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH} + \text{H}_2\text{O}$ , m.p. 201° (decomp.), is obtained by the action of acid on its benzylidene compound, which is itself the condensation product of benzaldehyde and glycocoll under the action of sodium hydroxide. A more soluble stereoisomeric acid, m.p. 187° (decomp.), is formed simultaneously (Erlenmeyer, Ann. 307, 84).

$\beta$ -Phenyl- $\beta$ -aminolactic acid, phenyl-isoserine,  $\text{C}_6\text{H}_5\text{CH}(\text{NH}_2)\cdot\text{CHOH}\cdot\text{COOH}$ , m.p. 231° (decomp.), is an isomer of the preceding compound, and is obtained as an addition product of ammonia on sodium phenyl-glycidate in the cold, or on  $\beta$ -phenyl- $\beta$ -bromo- $\alpha$ -hydroxypropionic acid (Oesterlin, C. 1929, II, 1398). Another stereoisomeric acid, m.p. 241°, is formed at higher temperatures (Erlenmeyer, Ber. 39, 791). Another isomeric acid, m.p. 270–280° (decomp.), has been obtained by treating phenyl-glycidic ester with ammonium hydroxide and hydrolysing the amide formed with barium hydroxide (Oesterlin, loc. cit.). For dihydroxy-serines, see Rosenmund, Ber. 52, 1734.

$\beta$ -Phenyl- $\beta$ -chloro- $\alpha$ -hydroxypropionic acid,  $\text{C}_6\text{H}_5\text{CHCl}\cdot\text{CH}(\text{OH})\cdot\text{COOH}$ , m.p. 141°, and phenyl- $\beta$ -bromo- $\alpha$ -hydroxypropionic acid (see above) are obtained by the action of the fuming hydrogen halides on phenyl-glyceric acid. *o*- and *p*-Nitro-phenyl- $\beta$ -chlorolactic acids, m.p. 125° and 167°, obtained from the corresponding glycidic acids by action of fuming HCl. *o*-Nitrophenyl- $\beta$ -bromolactic acid, m.p. 135° (Lipp, Ber. 16, 1290; 19, 2646; Morgan, Ber. 17, 221).

Cinnamic acid dichloride,  $\alpha, \beta$ -dichloro-hydrocinnamic acid,  $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CHCl}\cdot\text{COOH}$ , m.p. 163°, is obtained by the action of chlorine in carbon disulphide solution on cinnamic acid, or by the action of fuming HCl on phenyl-chlorohydroxypropionic acid (Erlenmeyer, Ber. 14, 1867). Allocinnamic acid dichloride is a viscous oil. It has been resolved by means of strychnine. Cinnamic acid dibromide,  $\alpha, \beta$ -dibromo-hydrocinnamic acid, m.p. 195°, breaks up on boiling with water, giving carbon dioxide, phenyl-acetaldehyde, cinnamic acid, and phenyl-bromohydroxypropionic acid. It has been resolved by means of strychnine. Methyl ester, m.p. 117°; ethyl ester, m.p. 76° (Sudborough, J. 83, 666). Allocinnamic acid dibromide, m.p. 91–93°, can be resolved by means of cinchonine. Methyl ester, m.p. 53° (Aronstein, Ber. 22, 1181; Laebermann, Ber. 26, 1664; 27, 2038).

*o*- and *p*-Nitro- $\alpha, \beta$ -dibromo-hydrocinnamic acids, m.p. 180° and 217°. *o*- and *p*-Ethyl esters, m.p. 71° and 110° (Drewson, Ann. 212, 151).

*o*-Methoxy-cinnamic acid dibromide, m.p. 175°; piperonyl-acrylic acid dibromide, m.p. 156°. In these two dibromides the bromine atom next to the benzene nucleus is exceedingly reactive, like that of the *pseudo*-phenyl halides and the dibromides of the olefine-phenols (Werner, Ber. 39, 27; Hoering, Ber. 40, 2174).

Phenyl-glycidic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{O}\cdot\text{CH}\cdot\text{COOH}$ , m.p. 84° (Dieckmann, Ber. 43,

1035), is obtained by the action of alkalis on phenyl-chloro-hydroxypropionic acids; by the action of hydrogen peroxide and alkali, or of hypohalites on cinnamic aldehyde at a temperature below 50° (Ger. Pats. 509,938 and 515,034; Fr. Pat. 682,471); and by condensation of benzaldehyde with chloroacetic ester by means of sodium ethylate or sodamide. It decomposes readily into carbon dioxide and phenyl-acetaldehyde. When boiled with water phenyl-glyceric acid is also produced. When acted upon with hot concentrated hydrochloric acid it partly rearranges into the isomeric phenyl-pyruvic acid (p. 428) (*Erlenmeyer*, Ber. 33, 3001). Its esters when warmed in the presence of catalysts, such as alumina, rearrange to so-called *formyl-phenyl-acetic esters* (p. 422) (*Tiffeneau*, An. Argent. 16, 144). Sodium salts of optically active phenyl-glycidic acids have been obtained from the optically active phenyl-bromo-hydroxypropionic acids.

A large number of homologous phenyl-glycidic esters have been obtained by condensing aromatic aldehydes and ketones with chloroacetic or  $\alpha$ -chloropropionic esters, with sodium ethylate or sodamide as condensing agent (*Darzens*, C.r. 139, 121; 142, 214; *Claisen*, Ber. 38, 699; *Rosenmund*, Ber. 52, 1734). The free acids, obtained by hydrolysis, readily decompose into carbon dioxide and aldehydes or ketones, in a similar manner to phenyl-glycidic acid itself (pp. 266, 281).  $\beta$ -Methyl- and  $\beta$ -ethyl-phenyl glycidic esters, b.p. 148° and 149° (12 mm.). The methyl ester has a strong odour of strawberries.  $\alpha$ -Methyl-phenyl-glycidic ester, b.p. 153° (18 mm.). Diphenyl-glycidic acid, m.p. 114–115°; ethyl ester, b.p. 210–215° (25 mm.) (*Rulowski*, Ber. 64, 693).

*o*-Nitrophenyl-glycidic acid,  $\text{NO}_2[\text{2}]\text{C}_6\text{H}_4\text{CH}\cdot\text{O}\cdot\text{CHCOOH} + \text{H}_2\text{O}$ , m.p. 125° (anhydrous), 94° (hydrated), is obtained by the action of alcoholic potash on *o*-nitrophenyl-chloro-hydroxypropionic acid. When heated it decomposes into carbon dioxide and indigo, and when boiled with water it gives anthranil and anthroxan-aldehyde (p. 407) (*Einhorn*, Ann. 284, 135; *Lipp*, Ber. 19, 2649).

$\gamma$ -Phenyl- $\alpha$ -hydroxybutyrolactone,  $\text{C}_6\text{H}_5\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\text{COO}$ , m.p. 125°, is obtained by reduction of benzoyl-pyruvic acid with sodium amalgam. When boiled with dilute hydrochloric acid it rearranges to  $\beta$ -benzoyl-propionic acid (p. 431) (*Erlenmeyer*, Ber. 35, 3767).

### (c) Trihydroxy-alcohol Acids

$\gamma$ -Phenyl-trihydroxy-butyric acid,  $\text{C}_6\text{H}_5(\text{CHOH})_3\text{COOH}$ , readily forms a lactone, m.p. 116°, which on reduction gives phenyl-tetrose (p. 403).  $\gamma$ -Phenyl-trihydroxy-butyric acid is obtained from the dibromide of cinnamic aldehyde cyanhydrin (*Fischer*, Ber. 25, 2556; *Thiele*, Ann. 319, 206).

## 7. Phenyl Paraffin Aldehyde Carboxylic Acids

In the chapters dealing with aliphatic unsaturated ketols, hydroxy-olefine carboxylic acids, and hydroxy-keto carboxylic acids (Vol. I, pp. 393, 452, 598), the formation of the so-called hydroxy-methylene compounds was explained. They are the condensation products of acetone, acetic acid, acetoacetic esters and other substances with formic ester in the presence of sodium ethylate. Formerly it was thought that these compounds contained an aldehydo-group, because in certain ways they react as aldehydes. They are, however, distinctly acidic in character, and this fact is best accounted for by regarding them as hydroxy-methylene compounds. It is noteworthy that in the condensation of phenyl-acetic ester with formic ester in the presence of sodium ethylate, two isomeric esters are formed. Both give the same compound with phenyl-hydrazine. Both, according to current views, consist chiefly of two stereoisomeric enol-forms, while the aldehyde form ("formyl-phenyl-acetic ester"), formerly attributed to the solid ethyl ester and to the methyl ester melting at 41°, seems only to exist in alcoholic solution (*Wislicenus*, Ann. 389, 265). One of the ethyl esters is a liquid, the other a solid. In solution, and on standing, they readily change into one another. In the metallic compounds the liquid form is present. It is distinguished from the solid form by giving a strong bluish-violet colouration with ferric chloride, and by more readily reacting with phenyl isocyanate.

**Methyl hydroxymethylene-phenyl-acetate**,  $\text{CHOH:C(C}_6\text{H}_5\text{)COOCH}_3$ , is obtained by condensing methyl phenyl-acetate and methyl formate with sodium in ether as condensing agent. Its  $\alpha$ -form, m.p.  $40-41^\circ$ , shows the typical reactions of an enol-compound, *viz.*, the coloration with ferric chloride, and formation of a sodium salt. On rapid acidification the  $\alpha$ -form changes to the  $\beta$ -form, m.p.  $91-93^\circ$ , which does not give the ferric chloride reaction, and is therefore to be regarded as an aido-form,  $\text{CHO}\cdot\text{CH(C}_6\text{H}_5\text{)COOCH}_3$ , or an aldo-enol form,  $\text{CHO}\cdot\text{C(C}_6\text{H}_5\text{):C(OH)OCH}_3$ . Methyl alcohol adds on to both forms, giving a compound, m.p.  $96-97^\circ$ . In solution, or on heating, the  $\beta$ -form changes into the  $\alpha$ -form, though the reverse change has not yet been observed to take place spontaneously (*Wislicenus*, Ann. 413, 206).

**Ethyl hydroxymethylene-phenyl acetate**, "formyl-phenyl-acetic ester,"  $\text{CHOH:C(C}_6\text{H}_5\text{)COOC}_2\text{H}_5$ ,  $\alpha$ -form, b.p.  $125-126^\circ$  (9 mm.),  $\beta$ -form, m.p.  $110^\circ$  (observed in a Jena glass capillary). The  $\alpha$ -ester is obtained from the reaction product of phenyl-acetic and formic esters with sodium ethylate, which is decomposed with carbon dioxide, followed by vacuum distillation of the precipitate. The  $\beta$ -form (formerly called the  $\gamma$ -form) is obtained from the  $\alpha$ -form by dissolving it in caustic potash and precipitating with dilute sulphuric acid. The form formerly called  $\beta$  has been found to be an impure  $\gamma$ -form (as formerly designated). It is extremely sensitive to traces of alkali, and when its melting point is determined in a capillary tube made of ordinary glass, it can be as low as  $70^\circ$ . The *phenylurethane* of the  $\alpha$ -form, m.p.  $59^\circ$ , appears, on heating, to change into that of the  $\beta$ -form, m.p.  $123-124^\circ$ . In alcoholic solution the solvent partly adds on to the double bond of the enol forms. In air, both forms undergo autoxidation to phenyl-glyoxylic acid and formic ester (*Scheiber*, Ann. 405, 295; *Dieckmann*, Ber. 49, 2213; 50, 1375; *Wislicenus*, Ber. 51, 1366). The sodium compound of the  $\alpha$ -ester gives an unstable liquid  $\alpha$ -benzoate with benzoyl chloride, which on distillation isomerises to the solid  $\beta$ -benzoate, m.p.  $88^\circ$ . **Hydroxymethylene-benzyl cyanide**,  $\text{CHOH:C(C}_6\text{H}_5\text{)CN}$ , m.p.  $158^\circ$ , is obtained from benzyl cyanide and isoamyl formate. On catalytic reduction it gives the aldime of hydroxymethylene-phenyl-acetaldehyde,  $\text{C}_6\text{H}_5\text{C(CH:NH)CHOH}$ , m.p.  $110^\circ$ , from which oxalic acid liberates the aldehyde, m.p.  $95^\circ$  (*Rupe*, Helv. 10, 299).

## 8. Phenyl Paraffin Keto-carboxylic Acids

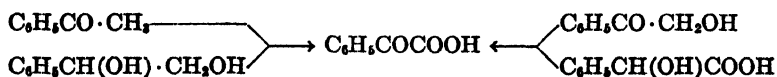
The phenyl-ketonic acids, like the aliphatic ketonic acids, can be classified into  $\alpha$ -,  $\beta$ -, and  $\gamma$ -acids, and each of these groups can be subdivided according to whether the keto-group is, or is not, directly attached to the ring. The general method of preparing (hydroxy-) phenyl-keto-carboxylic acids is to condense phenols with dicarboxylic acids by means of zinc chloride:  $(\text{HO})_2\text{C}_6\text{H}_4 + \text{HO}\cdot\text{CO}(\text{CH}_2)_n\text{COOH} = (\text{HO})_2\text{C}_6\text{H}_3\text{CO}(\text{CH}_2)_n\text{COOH}$ . By this method, long-chain benzoyl-aliphatic acids are obtained (Ger. Pat. 521,458). By reduction with amalgamated zinc and hydrochloric acid, phenyl keto-carboxylic acids are converted into phenyl-aliphatic acids.

### (a) $\alpha$ -Keto-carboxylic Acids

These are obtained by the oxidation of (1) ketones, (2) glycols, (3) keto-alcohols, and (4) hydroxy-carboxylic acids. Nuclear syntheses include (5) the hydrolysis of the cyanides of keto-acids by means of cold concentrated hydrochloric acid, and (6) the action of chloroxalic esters on benzene hydrocarbons in the presence of aluminium chloride.

**Phenyl-glyoxylic acid**, *benzoyl-formic acid*,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{COOH}$ , m.p.  $65^\circ$ , is isomeric with the phthalaldehyde-acids. It is obtained by the oxidation of acetophenone with potassium ferricyanide

(*Buchka*, Ber. 20, 389), or of phenyl-glycol, benzoyl-carbinol, or mandelic acid with nitric acid:



It is prepared by the oxidation of an aqueous solution of sodium mandelate with permanganate in the cold (*Corson*, Org. Synth. 8, 68).

It was first synthesised by *Claisen*, who prepared its nitrile, benzoyl cyanide, from benzoyl chloride by the action of mercury or silver cyanide, and then hydrolysed this nitrile. *Posner* (Ber. 53, 1925) prepared the ethyl ester by acting on chloroxalic ester with mercury diphenyl, or with benzene in the presence of aluminium chloride, and by passing oxides of nitrogen into an alkaline suspension of indigo.

Phenyl-glyoxylic acid is very soluble in water. It decomposes on distillation, mainly into carbon monoxide and benzoic acid, and to a lesser extent into carbon dioxide and benzaldehyde. When heated with aniline it breaks down into carbon dioxide and benzylidene-aniline (p. 272); this reaction also occurs smoothly with ring-substituted phenyl-glyoxylic acids, and can be used for the preparation of aldehydes. When treated with benzene containing thiophene and concentrated sulphuric acid, phenyl-glyoxylic acid and all its derivatives, including *isatin* (see p. 424), give a dark red colouration, which gradually changes to bluish-violet.

As a keto-acid, phenyl-glyoxylic acid combines with sodium bisulphite and with hydrocyanic acid (see phenyl-tartronic acid). When reduced with sodium- or zinc-amalgam it gives mandelic acid, and with hydrogen iodide it gives phenyl-acetic acid. With hydrogen sulphide it gives  $\text{S}(\text{SCH}(\text{C}_6\text{H}_5)\text{COOH})_2$ , which is converted by alkalis into **thiophenyl-acetic acid**,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{SH})\text{COOH}$ , an oil (*Ulpiani*, Lincei, 12, II, 219).

Methyl ester, b.p. 247°. Ethyl ester, b.p. 257°.  $\alpha$ -Amide, m.p. 90°.  $\beta$ -Amide hydrate,  $\text{C}_6\text{H}_5\text{COCO}\cdot\text{NH}_2 + \text{H}_2\text{O}$ , m.p. 64°.  $\gamma$ -Amide, m.p. 134° (*Claisen*, Ber. 12, 633; *Buchka*, Ber. 20, 397). The anilide, m.p. 63°, is obtained from  $\gamma$ -benzil-monoxime (*q.v.*) by the action of phosphorus pentachloride.

**Benzoyl cyanide**,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CN}$ , m.p. 34°, b.p. 96° (15 mm.), is obtained by distilling benzoyl chloride with mercury cyanide; by the action of benzoyl chloride on a solution of hydrocyanic acid in ether in the presence of pyridine, when its dimer is also produced; from isonitroso-acetophenone by the action of acetyl chloride (*Claisen*, Ber. 20, 2196; 31, 1023); from benzene by the action of gaseous cyanogen and aluminium chloride (*Vorländer*, Ber. 44, 2455); and from benzaldehyde cyanhydrin by the action of chromic acid in glacial acetic acid (Arch. Pharm. 269, 583). When its solution in dry ether is treated with sodium it is converted into *bis*-benzoyl cyanide,  $(\text{C}_6\text{H}_5\text{NO})_2$ , m.p. 95° (*Diels*, Ber. 41, 1893). Benzoyl cyanide is decomposed by alkalis into benzoic acid and potassium cyanide, and it is converted by concentrated hydrochloric acid into phenyl-glyoxylic acid. For its reactions with organo-magnesium compounds, see *de Coster*, Ac. Belg., 1925, 361. A trimolecular benzoyl cyanide  $(\text{C}_6\text{H}_5\text{NO})_3$ , forming yellow needles, m.p. 194°, is obtained by acting on benzoyl bromide with silver cyanide (*Diels*, Ber. 40, 1655).

$\omega$ -Trichloro-acetophenone,  $\text{C}_6\text{H}_5\text{COCOCl}_3$ , the chloride of benzoyl-orthoformic acid, b.p. 120–121° (15 mm.), is obtained from benzene and trichloro-acetonitrile by the action of aluminium chloride, followed by decomposing the product with gaseous hydrogen chloride (*Houben*, J. pr. 123, 313), and by way of its carbinol (obtained from benzene and chloral) by oxidation with dichromate. On boiling with alkalis it gives chloroform and benzoic acid (*Florence*, Bull. 49, 925).

**Chloro-isonitroso-acetophenone**, benzoyl-formoximic chloride,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}(\text{:NOH})\text{Cl}$ , m.p. 131°, is a chlorination product of isonitroso-acetophenone (p. 407) (*Claisen*, Ann. 274, 95). **Formazyl-phenyl ketone**,  $\text{C}_6\text{H}_5\text{COC}(\text{N}:\text{NC}_6\text{H}_5):\text{NNHC}_6\text{H}_5$ , m.p. 142°, is obtained from benzoyl-acetic acid, or benzoyl acetone, by the action of an aqueous solution of a diazonium salt. When reduced it



breaks down into aniline and benzoyl-amidrazone,  $C_6H_5CO \cdot C(NH_2):NNHC_6H_5$ , m.p.  $152^\circ$  (Bamberger, J. pr. 65, 139).

Benzoyl cyanide anil,  $C_6H_5C(:NC_6H_5)CN$ , m.p.  $72^\circ$ , has been obtained from anilino-phenyl-acetonitrile (p. 413) by oxidation with permanganate in acetone. *p*-Dimethyl-amino-benzoyl cyanide anil, m.p.  $121^\circ$ , is obtained in a similar manner (Sachs, Ber. 35, 3569).

Phenylhydrazimethylenecarboxylic acid, hydrazine salt, m.p.  $119^\circ$ . Di-phenyl-glyoxylic hydrazone,  $N_2:C(C_6H_5)COOH_2$ ; diethyl ester, m.p.  $138^\circ$  (Curtius, J. pr. 44, 567). Phenyl-glyoxylic-phenylhydrazone, m.p.  $153^\circ$  (Elbers, Ann. 227, 341).

$\beta$ - or *syn*-Phenylglyoxylic oxime, m.p.  $147^\circ$ ;  $\alpha$ - or *anti*-phenylglyoxylic oxime, isonitroso-phenylacetic acid,  $C_6H_5 \cdot C(:NOH)COOH$ , m.p.  $128^\circ$  (Hantzsch, Ber. 24, 42). Methyl ester, m.p.  $138^\circ$ ; dimethyl ester, m.p.  $56^\circ$  (Gabriel, Ber. 16, 519). Benzoyl cyanide oxime, isonitroso-benzyl cyanide,  $C_6H_5 \cdot C(:NOH)CN$ , m.p.  $129^\circ$ , is obtained by the action of amyl nitrite and sodium ethylate on benzyl cyanide, from phenylglyoxime by boiling with sodium carbonate, or directly from  $\omega$ -dibromo-acetophenone by the action of hydroxylamine and alkali (Rissanow, Ber. 24, 3504; Zimmermann, J. pr. 66, 353).

Substituted benzoyl-formic acids. (Poly)-hydroxy-benzoyl formic esters are obtained from phenols and ethyl cyanoacetate by the action of zinc chloride (Finger, J. pr. 103, 249). *p*-Methoxy-benzoyl cyanide, m.p.  $63-64^\circ$ ; 3,4-dimethoxy benzoyl cyanide, m.p.  $116-117^\circ$ ; 3,4-methylene-dioxy-benzoyl cyanide, m.p.  $98-99^\circ$ , are obtained from the corresponding aldehydes (Arch. Pharm. 269, 581). *o*- and *p*-Bromobenzoyl-formic acids, m.p.  $93-103^\circ$  and  $108^\circ$  (Rissanow, Ber. 25, 3298; Rupe, Ber. 28, 259).

*o*-Nitrophenyl-glyoxylic acid,  $NO_2C_6H_4CO \cdot COOH + H_2O$ , m.p.  $47^\circ$ , anhydrous  $156-157^\circ$  (decomp.), is obtained (1) from *o*-nitrobenzoyl chloride, which is converted into the cyanide and then hydrolysed by Claisen's method (see above); (2) from *o*-nitromandelic acid by the action of permanganate (Heller, Ber. 44, 2418). Ethyl ester, m.p.  $43-44.5^\circ$ ; amide m.p.  $199^\circ$ ; nitrile, m.p.  $54^\circ$  (Fehrlin, Ber. 23, 1577). With water its oxime gives carbon dioxide and *o*-nitrobenzonitrile, and with boiling aqueous alkali, salicylic acid (Meyer, Ber. 26, 1252). The acid forms two isomeric phenylhydrazones (Auwers, Ber. 23, 2080). *m*-Nitrophenyl-glyoxylic acid, m.p.  $77^\circ$ ; amide, m.p.  $151^\circ$ ; nitrile, b.p.  $230^\circ$  (145 mm.) (Claisen, Ber. 12, 1943). *p*-Nitrobenzoyl cyanide, m.p.  $116^\circ$ , is obtained from isonitroso-*p*-nitrobenzyl cyanide by decomposition (Zimmermann, J. pr. 66, 353).

Isatinic acid, *o*-aminobenzoyl-formic acid, or *o*-aminophenyl-glyoxylic acid, is obtained by reduction of *o*-nitrobenzoyl-formic acid with ferrous sulphate and caustic soda, and by the action of alkalis on isatin. When it is liberated from its lead salt with hydrogen sulphide and dried by evaporation in a good vacuum, it is obtained as a white powder. When heated in solution it quickly forms a lactam or a lactim.

Isatin, the lactam of isatinic acid,  $C_6H_4 \begin{matrix} \swarrow [1]CO \cdot CO \\ \searrow [2]NH \end{matrix}$ , or the lactim of isatinic acid,  $C_6H_4 \begin{matrix} \swarrow CO \\ \searrow N= \end{matrix} COH$ , m.p.  $201^\circ$ , was first obtained

by the oxidation of indigo. It forms orange-red prisms. It dissolves in alkalis forming salts. These solutions are first violet, but soon turn yellow, owing to the formation of isotinates. At the same time, isatin gives the reactions of a typical ketone. It is obtained from isonitroso-acetanilide,  $C_6H_5NH \cdot COCH:NOH$ , by the action of

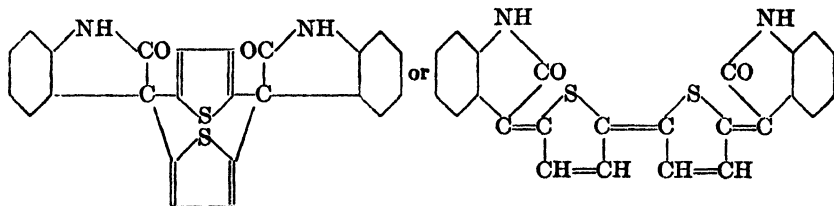
sulphuric acid when  $\beta$ -isatin-imine,  $C_6H_4 \begin{matrix} \swarrow NH \\ \searrow C= \end{matrix} CO$ , is formed. This is then acted upon with ammonia (Ger. Pat. 320,647).

Isatin is prepared by heating isonitroso-acetanilide (obtained from aniline by the action of chloral hydrate and hydroxylamine hydrochloride) with concentrated sulphuric acid (*Marvel, Org. Synth.* 1, 321). Other methods by means of which isatin and its derivatives may be obtained will be dealt with in the next volume under hydro-indole derivatives. Derivatives of both tautomeric forms are known, those from the lactam form being called *pseudo-* or *N-isatin* derivatives. While *Baeyer* held that free isatin had the lactim formula, recent investigations have shown that it has the lactam form both in the crystalline state, and in alcoholic solution (*cf.* Vol. IV).

Isatin was discovered by *Laurent* in 1841 (*C.r.* 12, 537) who obtained it by the action of nitric acid on indigo, but did not disclose the method. *O. L. Erdmann* (*J. pr.* [1], 24, 2) then published its preparation by means of chromic acid. As early as 1840, *Erdmann* had obtained chloro-derivatives of isatin by treating indigo with chlorine (*ibid.*, 19, 321; 22, 257).

Like pyrrole and other compounds containing a 5-membered ring, isatin shows a tendency to take up atoms or groups with the formation of 6-membered heterocyclic compounds. Thus, with diazomethane, 2,3-dihydroxy-quinoline, and with nascent oxygen at 50°, *isatoic anhydride* (p. 324) are formed.  $\alpha$ -Isatoxime,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C}(\text{NOH})$ , on heating with alkali, isomerises to *benzoylene-urea*,  
 $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \quad \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \quad \text{CO} \end{array}$  (*Heller, Ber.* 49, 2774). With thiophene in the presence of sulphuric acid, isatin condenses to give *indophenine*, which is formulated at present as:



(*Steinkopf, Ann.* 432, 251; 495, 144; *cf. Heller, Chem. Z.* 54, 986; 57, 74).

With ammonia, isatin forms a stable ketimine, *imesatin*, of which the formula has been given above. It forms dark yellow prisms, m.p. 175–176°. A highly

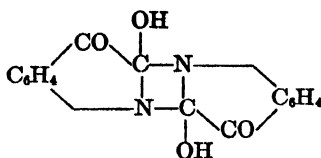
unstable addition product, known as *isatin-ammonia*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \\ \text{C}(\text{OH})(\text{NH}_2) \end{array}$ , is

also formed. It is orange in colour (*Reissert, Ber.* 57, 972). With ketones, such as acetone or acetophenone, in presence of alkali, isatin and isatinates condense, with enlargement of the ring. Salts of substituted cinchoninic acids are formed, *e.g.*, 2-phenyl-quinoline-4-carboxylic acid with acetophenone (*Dilthey, Ber.* 58, 1588). *N*-Substituted isatins have been obtained by condensing monosubstituted anilines with oxalyl chloride, followed by treatment with aluminium chloride (*Stollé, Ber.* 46, 3915); or *N*-substituted cyano-formanilides,  $\text{C}_6\text{H}_4\text{N}(\text{R})\text{COCN}$ , may be condensed by means of zinc chloride or aluminium chloride, and the imide

compound formed,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NR} \\ \diagup \quad \diagdown \\ \text{C:NH} \end{array} \text{CO}$ , is hydrolysed (*Ger. Pat.* 515,542).

The methods of formation, and reactions of isatin derivatives will be dealt with more fully in Vol. IV.

**Polymeric isatins.** When isatin-*O*-methyl ether is heated, or exposed to light, derivatives of a *bimolecular isatin* (*isatoid*) are formed. *Isatoid* itself:



m.p. 210–211°, is obtained by heating isatol.  $\alpha$ -Isatol, red prisms, m.p. 194.5°, and  $\beta$ -isatol, orange-yellow crystals, m.p. 162–163.5°, are trimolecular isatins, obtained by the action of benzoyl chloride on the silver compound of isatin (Heller, Ber. 54, 2217; J. pr. 135, 22; Hantzsch, J. pr. 115, 127).

**N-Hydroxy-isatin**,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{NOH} \end{array}$  or  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{N} \end{array} \text{C}=\text{O} \cdot \text{OH}$ , forms orange-red

needles, strikingly resembling isatin, and melting at the same temperature, of 200–201°. It is obtained by the action of acids on *o*-nitrobenzoyl-diazomethane,  $\text{NO}_2\text{C}_6\text{H}_4\text{COCHN}_2$ , in glacial acetic acid (Arndt, Ber. 60, 1367). For other methods of preparation, see a pamphlet by Heller, Isatin, etc., Stuttgart, p. 74 (1931). When acted upon by alkali, it is converted into anthroxanic acid (see below).

**Formyl-isatinic acid**,  $\text{HCO} \cdot \text{NH}[2]\text{C}_6\text{H}_4\text{COCOOH}$ , m.p. 144° (not quite definite). **Acetyl-isatinic acid**,  $\text{CH}_3\text{CO} \cdot \text{NH}[2]\text{C}_6\text{H}_4\text{COCOOH}$ , m.p. 160°, is obtained from *N*-acetyl-isatin (see below) by acting on it first with alkalis, then with acids. **Benzoyl-isatinic acid**, m.p. 188°, is obtained by the action of permanganate on benzoyl-tetrahydroquinoline. **Formyl-isatin**,  $\text{C}_6\text{H}_4 \begin{array}{c} [1] \text{CO} \cdot \text{CO} \\ [2] \text{N} - \text{CHO} \end{array}$ , m.p.

108°. **Acetyl-isatin**,  $\text{C}_6\text{H}_4 \begin{array}{c} [1] \text{CO} \cdot \text{CO} \\ [2] \text{N} - \text{COCH}_3 \end{array}$ , m.p. 141°. **Benzoyl-isatin**, m.p.

206°. **Benzene-sulpho-isatin**, m.p. 187°, and ***N*-isatin carbonic ester**, m.p. 117°, are obtained from sodio-isatin and benzenesulphonyl chloride, and ethyl chloro-carbonate, respectively (Schooten, Ber. 24, 772; Heller, Ber. 51, 424; Hantzsch, Ber. 57, 195).

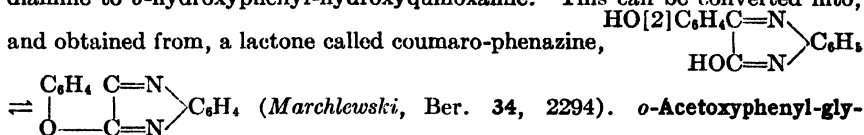
**Anthroxanic acid**,  $\text{C}_6\text{H}_4 \begin{array}{c} [1] \text{C} - \text{COOH} \\ [2] \text{N} \end{array} \text{O}$ , m.p. 190°, is obtained, together with

other products, when isatinic acid is oxidised with permonosulphuric acid, or by the reduction of *o*-nitrophenyl-glyoxylic acid with tin and acetic acid, or zinc dust and ammonia; in the latter reaction the unstable *o*-hydroxylamino-phenyl-glyoxylic acid is formed intermediately (Bamberger, Ber. 43, 122) (cf. the similar methods of preparing anthranil, p. 278). *o*-Hydroxylamino-phenylglyoxylic acid gives two anhydrides, i.e., anthroxanic acid and *N*-hydroxy-isatin (see above). If a caustic alkali is added to the latter, an intense violet colour is formed momentarily, due to the formation of a *N*-hydroxy-isatin salt, and then the solution turns reddish-yellow and contains an *o*-hydroxyl-amino-phenyl-glyoxylate, which, when acidified, reforms *N*-hydroxy-isatin. When the alkaline solution is heated, or allowed to stand, it becomes colourless, and now contains an anthroxanate. On acidifying, the acid separates as a colourless precipitate (Arndt, Ber. 60, 1368). This is the usual method of preparing anthroxanic acid. It can also be obtained, however, by heating *o*-nitroso-mandelic nitrile with concentrated hydrochloric acid (Heller, Ber. 39, 2344), and by oxidising anthroxanaldehyde with permanganate (Schilling, Ber. 16, 2222). When heated with water to 150°, it breaks down giving chiefly aniline, and a little anthranil and carbon dioxide (Bamberger, J. pr. 81, 254). Methyl ester, m.p. 70°; ethyl ester, m.p. 64–65° (Heller, Ber. 44, 2421).

***p*-Dimethyl-aminophenyl-glyoxylic ester**,  $(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_4\text{COCOOCC}_2\text{H}_5$ , m.p. 187°, is obtained by the action of dimethylaniline on ethyl oxalate or ethyl oxaly chloride in the presence of aluminium chloride (Michler, Ber. 10, 2081; Guyot, C.r. 144, 1120). Its chloride is obtained by the action of dimethylaniline on

oxalyl chloride. On heating it breaks down into carbon monoxide and *p*-dimethylamino-benzoyl chloride (*Staudinger*, Ber. 42, 3486). *p*-Aminophenyl-glyoxylic acid and its *N*-alkyl derivatives are obtained from aminophenyltartronic acids (p. 436) by oxidation (Ger. Pats. 117,021 and 117,168).

*o*-Hydroxyphenyl-glyoxylic acid,  $\text{HO}[2]\text{C}_6\text{H}_4\text{COCO}_2\text{H}$ , m.p. 57°, is obtained from isatinic acid by means of the diazo-sulphate. It condenses with *o*-phenylene diamine to *o*-hydroxyphenyl-hydroxyquinoxaline. This can be converted into,



*o*-Acetoxyphenyl-glyoxylic acid, m.p. 101–106° (containing 1 mol.  $\text{H}_2\text{O}$ ), is obtained from its nitrile, m.p. 111°, which is the reaction product of aceto-salicyl chloride and silver cyanide (*Änschütz*, Ann. 368, 80).

**Coumaran-dione**,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CO}$ , yellow needles, the oxygen analogue of isatin, m.p. 134°, is obtained by the oxidation of the so-called oxy-indigo with chromic acid in glacial acetic acid (*Stoermer*, Ber. 42, 199). A derivative,

*isonitroso-coumarone*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C:NOH}$ , m.p. 172° (decomp.), is obtained

from  $\alpha$ -nitro-coumarone, by a rearrangement which occurs in the presence of sodium ethoxide (*Stoermer*, Ber. 35, 1640; *Fritsch*, *ibid.*, 4346). The *p*-dimethyl-

amino-anil of coumaran-dione,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C:NC}_6\text{H}_4\text{N}(\text{CH}_3)_2$ , m.p. 185°, is

obtained by the condensation of coumaranone with *p*-nitroso-dimethylaniline. The two last-named compounds are decomposed by hydrochloric acid into hydroxylamine and *p*-amino-dimethylaniline, and *o*-hydroxyphenyl-glyoxylic acid, respectively (*Fries*, Ber. 44, 124).

**Thionaphthene-quinone**, "thio-isatin,"  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{CO}$ , crystallises from alcohol in yellow prisms, m.p. 121°, b.p. 247°. It is obtained from its  $\alpha$ -anil, which is a transformation product of dibromo-thioindoxyl,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CBr}_2$ , or from

*isonitroso-thioindoxyl*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C:NOH}$ , m.p. 172°, by decomposition with

dilute sulphuric acid. It dissolves in alkalis, salts of *thiophenol-o*-glyoxylic acid being formed. The free acid easily reverts to the anhydride (*Bezfrick*, Ber. 41, 227). Coumaran-dione and thionaphthene-quinone are dealt with further in the next volume.

*p*-Methoxyphenyl-glyoxylic acid, m.p. 89°, veratroyl-carboxylic acid,  $(\text{CH}_3)_2\text{[3,4]C}_6\text{H}_2\text{CO}\cdot\text{COOH}$ , m.p. 138°, and piperonyl-carboxylic acid,  $(\text{CH}_2\text{O}_2)\text{[3,4]C}_6\text{H}_2\text{CO}\cdot\text{COOH}$ , m.p. 148°, have been obtained by the oxidation of anethole, isoeugenol-methyl ether, and isosafrol, respectively (*Wagner*, Ber. 24, 3488). The nitriles of the first two acids, m.p. 64° and 117°, have been prepared from anisic and veratroyl chlorides and hydrocyanic acid in the presence of pyridine (*Mauthner*, Ber. 42, 188). 2,5-Dihydroxyphenyl-glyoxylic acid, m.p. 141°, is obtained by oxidising *o*-hydroxyphenyl-glyoxylic acid with potassium persulphate in alkaline solution (*Neubauer*, Physiol. 52, 375).

**Homologous phenyl-glyoxylic acids.** Methyl-isatin,  $\text{CH}_3[5]\text{C}_6\text{H}_3 \begin{array}{l} \text{[1]CO}\cdot\text{CO} \\ \text{[2]NH} \end{array}$ , m.p. 184°, is derived from *m*-tolyl-glyoxylic acid. It is prepared from *p*-methyl-isatin-*p*-tolyl-imide, m.p. 259°, which is the reaction product of dichloroacetic acid and *p*-toluidine, by boiling with hydrochloric acid (*Meyer*, Ber. 16, 2261; *Duisberg*, Ber. 18, 198).

*p*-Tolyl-glyoxylic acid, m.p. 96° (*Claus*, Ber. 20, 2048).

(*p*) 2,5-Xylyl-glyoxylic acid, m.p. 75° (*Bouveault*, Bull. [3], 17, 940).

(*m*) 2,4-Xylyl-glyoxylic acid, m.p. 75° (*Bouveault*, Bull. [3], 17, 369).

(*o*) 3,4-Xylyl-glyoxylic acid, m.p. 92° (*Buchka*, Ber. 20, 1766).

Mesityl-glyoxylic acid, m.p. 118° (*Claus*, J. pr. 41, 504).

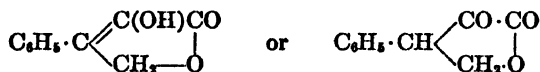
2,4,5-Pseudocumyl-glyoxylic acid, m.p. 75° (*Claus*, *ibid.*).

2,3,4,6- and 2,3,5,6-Tetramethylphenyl-glyoxylic acid (*Claus*, Ber. 19, 233; 20, 3099). Cymyl-glyoxylic acid (*Bouveault*, Bull. [3], 17, 940).

Phenyl-pyruvic acid,  $C_6H_5 \cdot CH_2CO \cdot COOH$ , m.p. 157°, with loss of carbon dioxide. It is obtained: from  $\alpha$ -benzoyl-aminocinnamic acid, by boiling with aqueous caustic alkali or hydrochloric acid; from phenyl-oxaloacetic ester by boiling with dilute sulphuric acid; by a rearrangement of phenyl-glycidic acid (p. 421); and from benzyl cyanide and ethyl oxalate, the phenyl-cyanopyruvic ester first formed being hydrolysed with cold conc. sulphuric acid (*Erlenmeyer*, Ann. 271, 163; 275, 8; *Hemmerlé*, Ann. chimie [9], 7, 226). The enol form,  $C_6H_5CH:C(OH)COOH$ , is assigned to the free acid, and the keto-form to the salts (*Bouveault*, C.r. 160, 100). The acetate of the enol form, m.p. 168°, is obtained from the acid or its sodium salt by means of acetic anhydride. With ammonia, it is converted into  $\alpha$ -phenacetyl-amino-hydrocinnamic acid or phenacetyl-phenylalanine (p. 414). It is smoothly decomposed by hydrogen peroxide in alkaline solution into carbon dioxide and phenylacetic acid. It combines with benzaldehyde in the presence of hydrochloric acid to give  $\beta,\gamma$ -diphenyl- $\alpha$ -keto-butyrolactone (p. 571) (*Erlenmeyer*, Ann. 333, 160). There are three isomeric forms of the esters; the unstable  $\alpha$ -form of the ethyl ester, m.p. 51–52°, on slow distillation changes to the stable  $\beta$ -form, an oil, b.p. 149° (15 mm.); these two are obtained from phenyl-cyanopyruvic ester or phenyl-hydroxymaleinimide at 140° by the action of alcoholic sulphuric acid. The  $\gamma$ -form, m.p. 79°, is obtained from the  $\beta$ -form by means of sodium acetate solution. The  $\alpha$ - and  $\beta$ -forms are enolic, and the  $\gamma$ -form is keto (*Gault*, C.r. 171, 395).

The methyl ester, m.p. 75°, and the ethyl ester, m.p. 45° (51–52°?), combine with sodium bisulphite. Under the action of alkalis, the esters polymerise to di-phenyl-pyruvic acid,  $C_6H_5CH_2C(OH)(COOH)CH(C_6H_5)CO \cdot COOH$ , m.p. 194° (decomp.). The acid itself polymerises less readily (*Hemmerlé*, C.r. 162, 758).

$\alpha$ -Oximino- $\beta$ -phenyl-propionic acid,  $C_6H_5CH_2C(NO)COOH$ , m.p. 159–160° (decomp.), is obtained by the action of 90% sulphuric acid, and nitrosyl-sulphuric acid, on benzyl-acetoacetic ester, followed by hydrolysis of the product. It gives  $\alpha$ -hydroxy- $\beta$ -phenyl-crotonolactone:



when boiled with formaldehyde and hydrochloric acid (*Hall*, J. 107, 132).

*o*-Hydroxyphenyl-pyruvic acid,  $HO \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot COOH$ , is obtained in a similar way to phenyl-pyruvic acid, from  $\alpha$ -benzoylamino-*o*-hydroxycinnamic acid, by the action of sodium hydroxide. Immediately it is produced it goes over

into its lactone,  $\alpha$ -oxo-dihydro-coumarin,  $C_6H_4 \begin{array}{l} \diagup [1]CH_2CO \\ \diagdown [2]O-CO \end{array}$ , m.p. 152° (*Erlenmeyer*, Ann. 357, 289).

The nitro-derivatives of phenyl-pyruvic acid are obtained by condensing ethyl oxalate with *o*- and *p*-nitrotoluenes by means of sodium hydroxide. *o*-Nitrophenyl-pyruvic acid,  $NO_2[2]C_6H_4CH_2COCOOH$ , m.p. 121°, on reduction gives first *N*-hydroxy-indole-, and then  $\alpha$ -indole-carboxylic acid,

$C_6H_4 \begin{array}{l} \diagup NH \\ \diagdown CH \end{array} C \cdot COOH$ . *p*-Nitrophenyl-pyruvic acid, m.p. 194°. *o,p*-, and *o,m*-

Methyl-nitrophenyl-pyruvic acids, m.p. 145° and 193° (*Reissert*, Ber. 30, 1030; 31, 387). *p*-Methoxy-*o*-nitrophenyl-pyruvic acid, m.p. 144–145° (with benzene of crystallisation, m.p. 80°), is obtained from *o*-nitro-*p*-tolyl ether (*Kermack*, J. 119, 1602).

**Benzyl-pyruvic acid**,  $C_6H_5CH_2CH_2COCO_2H + 1\frac{1}{2} H_2O$ , m.p.  $47^\circ$ , is obtained by a rearrangement of  $\alpha$ -hydroxyphenyl-crotonic acid, or preferably of its amide, by means of sodium hydroxide. With hydrochloric acid, the isomeric benzoyl-propionic acid is formed (p. 431). Benzyl-pyruvic acid is also obtained by the decomposition of benzyl-oxalo-acetic ester (p. 438) (*Wieland*, Ber. 31, 3134).  $\alpha,\alpha$ -Dibromo- and diiodo-phenyl-butyric acids,  $C_6H_5CH_2CH_2CX_2\cdot COOH$ , m.p.  $134^\circ$  and  $145^\circ$ , are obtained from the semi-carbazone of benzyl-pyruvic acid by the action of hypobromite and hypoiodite, respectively (*Bougault*, C.r. 163, 481). **Phenyl-ketene-carboxylic methyl ester**,  $C_6H_5C(:CO)COOCH_3$ , a bright-yellow oil, b.p.  $81-82^\circ$  (0.25 mm.), has been prepared by *Staudinger* (Ber. 50, 1024) from phenyl-malonic dimethyl ester, by heating it in a sealed tube at  $200^\circ$ .

### (b) Phenyl Paraffin $\beta$ -Keto-carboxylic Acids

**Formation.**—(1) Esters of benzoic acid condense with aliphatic esters in the presence of sodium ethoxide, with loss of alcohol. The process is similar to that involved in the formation of acetoacetic ester. Acetophenone, too, will condense with ethyl carbonate under similar conditions. (2) By means of aryl chlorides, such as benzyl chloride, aryl residues can be introduced into acetoacetic ester (see benzyl-acetic ester, below). Other methods of formation are: (3) the action of benzaldehydes on diazoacetic ester (see benzoyl-acetic ester, below). (4) the action of benzene on the chlorides of malonic hydrogen esters in the presence of aluminium chloride (*Marguery*, Bull. [3], 33, 548); (5) by the action of benzoyl chloride or bromide on magnesium- $\alpha$ -halogeno-aliphatic esters (*Meyer*, Ann. 347, 71); (6) the hydration of phenyl-propionic ester (p. 479).

**Reactions.**—With hydroxylamine they give oxime anhydrides, lactoximes, or isoxazolones; with hydrazine and phenylhydrazine, they give hydrazine anhydrides, lactazams, or pyrazolones. Their nitriles, the  $\beta$ -ketocyanides, are obtained from  $\omega$ -bromo-acetophenones by the action of aqueous-alcoholic KCN, and the keto-thiocyanates are prepared in a similar manner.

**Benzoyl-acetic acid**,  $C_6H_5\cdot CO\cdot CH_2\cdot COOH$ , melts at  $103^\circ$ , decomposing into carbon dioxide and acetophenone. It decomposes in the same way when boiled with dilute acids. It is obtained from its ethyl ester by hydrolysis with caustic potash at the ordinary temperature. It gives a violet-red coloration with ferric chloride.

**Ethyl benzoyl-acetate**,  $C_6H_5\cdot CO\cdot CH_2COOC_2H_5$ , b.p.  $148^\circ$  (11 mm.). **Formation:** (1) It was first obtained by *Weltner* (Ber. 17, 66) from ethyl phenyl-propiolate, by dissolving the latter in sulphuric acid and diluting with water. (2) Sulphuric acid is allowed to act on  $\alpha$ -bromo-cinnamic ester (*Michael*, Ber. 19, 1392). (3) The best methods of preparation are the condensation of ethyl benzoate and ethyl acetate by means of dry sodium ethoxide or sodium (*Claisen*, Ber. 20, 653, 2179; *Wahl*, Bull. 13, 265), and (4) the action of ammonia on C-benzoyl-acetoacetic ester (p. 434) obtained by the action of benzoyl chloride on sodio-acetoacetic ester (*Claisen*, Ann. 291, 70). (5) Small quantities are formed when acetophenone and ethyl carbonate are treated with sodium ethoxide; (6) by the action of diazoacetic ester on benzaldehyde (*Buchner*, Ber. 18, 2373); (7) by action on the chloride of hydrogen ethyl malonate with benzene and aluminium



(Holtzwar, J. pr. 39, 230). With hydroxylamine hydrochloride it gives phenyl-imido-isoxazolone,  $O \cdot N : C(C_6H_5) \cdot CH_2C(NH)$ , m.p.  $111^\circ$ , the imino-group being replaced by the oximino-group and the latter attaching itself to the cyano-group (Burns, J. pr. 58, 129). For *o*-, *m*-, and *p*-methoxy-benzoyl-acetic esters and their condensation to pyrazolones see Wahl, Bull. 11, 61. 3,4,5-Trimethoxy-benzoyl-acetic ester is obtained from trimethylgallic ester, ethyl acetate and sodium methylate. With sulphuric acid it undergoes ketolysis to trimethyl-gallacetophenone (p. 352) (Mauthner, J. pr. 112, 270).

*o*-Chlorobenzoyl-acetic ester cannot be distilled *in vacuo* without decomposition. *p*-Chlorobenzoyl-acetic ester, m.p.  $38^\circ$ . These compounds are obtained from sodio-acetoacetic ester and *o*- and *p*-chlorobenzoyl chlorides (Thorpe, Am. 37, 1258).

*p*-Nitrobenzoyl-acetic acid is obtained from nitrophenyl-propionic ester (Perkin, Ber. 17, 326) by the action of sulphuric acid. It melts at  $135^\circ$  with decomposition into carbon dioxide and *p*-nitro-acetophenone. The ester of *o*-nitrophenyl-propionic acid readily changes into the isomeric isatogenic ester. The nitro-benzoyl-acetic esters, *o*-, a liquid, *m*-, m.p.  $79^\circ$ , and *p*-, m.p.  $75^\circ$ , are best prepared by the decomposition of *o*-, *m*-, and *p*-nitrobenzoyl-acetoacetic esters (Bülow, Ber. 35, 931; Needham, J. 85, 148).

$\alpha$ -Methyl-benzoyl-acetic ester, b.p.  $226^\circ$  (225 mm.), gives  $\alpha$ -isonitroso-propionophenone with nitrous acid (Pechmann, Ber. 21, 2119).  $\alpha$ -Ethyl- and diethyl-benzoyl-acetic esters, b.p.  $210^\circ$  (90 mm.) and  $223^\circ$  (150 mm.). Allyl-benzoyl-acetic ester, b.p.  $220^\circ$  (100 mm.). Benzoyl-cyclopropane-carboxylic acid,

$C_6H_5COC\left(\begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix}\right)COOH$ , m.p.  $148^\circ$ , decomposes at a higher temperature into carbon dioxide and benzoyl-cyclopropane (Baeyer, Perkin, Ber. 16, 2128, 2136).

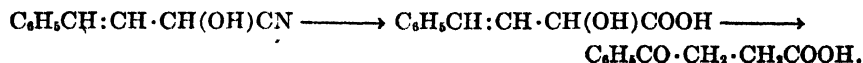
$\alpha$ -Phenyl-acetoacetic ester,  $C_6H_5CH(COCH_3)COOC_2H_5$ , b.p.  $146^\circ$  (11 mm.), is obtained by the action of sodium ethylate on its nitrile,  $C_6H_5CH(COCH_3)CN$ , m.p.  $90^\circ$ , the condensation product of benzyl cyanide and acetic ester (Beckh, Ber. 31, 3160). Propionyl-phenylacetic-ester,  $C_6H_5CH(COCH_2CH_3)COOC_2H_5$ , b.p.  $155^\circ$  (18 mm.), and propionyl-benzyl cyanide, m.p.  $70^\circ$ , are prepared in a similar manner (Dimroth, Ber. 36, 2242).

$\alpha$ -2,5-Dinitrophenyl-, and 2,4,6-trinitrophenyl-acetoacetic esters, m.p.  $94^\circ$  and  $98^\circ$ , are obtained from 2,5-dinitro-bromo-benzene and from 2,4,6-trinitro-chlorobenzene, respectively, by the action of sodio-acetoacetic ester (Jackson, Ber. 22, 990; Heckmann, Ann. 220, 131; Dittrich, Ber. 23, 2720).

Benzyl-acetoacetic ester,  $C_6H_5CH_2 \cdot CH \begin{smallmatrix} COOC_2H_5 \\ | \\ COCH_3 \end{smallmatrix}$ , b.p.  $276^\circ$ , is obtained by the action of benzyl chloride on sodio-acetoacetic ester (Conrad, Ann. 204, 179), and gives benzyl-acetone (Ceresole, Ber. 15, 1875) on ketonic hydrolysis, and  $\beta$ -phenyl-propionic acid on acid hydrolysis. For its electrolytic reduction, see Tafel, Ber. 40, 3312. *o*-Nitrobenzyl-acetoacetic ester, b.p. about  $180^\circ$  (1 mm.), is a brownish-yellow oil, obtained by the action of *o*-nitrobenzyl chloride on sodio-acetoacetic ester (Gabriel, Ber. 56, 1024).

### (c) γ- and δ-Keto-carboxylic Acids

$\beta$ -Benzoyl-propionic acid,  $C_6H_5 \cdot CO \cdot CH_2CH_2COOH$ , m.p.  $116^\circ$ , is obtained: (1) by the condensation of benzene and succinic anhydride by means of aluminum chloride (Cluvs, Ber. 20, 1376; Limpricht, Ann. 312, 110); (2) by the condensation of benzaldehyde with maleic or fumaric acid by means of piperidine at  $150$ – $160^\circ$  (Mayrhofer, Mo. 24, 80); (3) by the reduction of  $\beta$ -benzoyl-acrylic acid (p. 487); (4) from benzoyl-isosuccinic acid (p. 437) by loss of carbon dioxide; (5) from phenacyl-benzoyl-acetic ester by acid hydrolysis; and (6) from the addition product of hydrocyanic acid and cinnamic aldehyde by boiling with dilute hydrochloric acid; on careful hydrolysis in the cold phenyl-hydroxycrotonic acid is the first product, and this rearranges when boiled with hydrochloric acid or alkali (Bougault, C.r. 157, 403; Fittig, Ber. 29, 2582; Ann. 299, 23):





(7) Benzoyl-propionic acid is also obtained by a rearrangement of  $\gamma$ -phenyl- $\alpha$ -hydroxybutyrolactone (p. 421) (*Erlenmeyer*, Ber. 36, 2529); and (8) from sodio-acetophenone and iodoacetic ester (*Haller*, C.r. 153, 145).

Benzoyl-propionic acid gives **phenyl- $\Delta^2$ -crotonolactone**,  $C_6H_5C:CH:CH_2COO$ , m.p.  $91^\circ$ , by loss of water. The isomeric phenyl- $\Delta^1$ -crotonolactone,  $C_6H_5\cdot$ -

$CH:CH:CH\cdot COO$ , an oil, obtained from the dibromide of cinnamic aldehyde cyanhydrin very readily passes into the  $\Delta^1$ -lactone. Both are converted into benzoyl-propionic acid by hydrochloric acid, but behave differently toward permanganate, with which the  $\Delta^1$ -lactone gives phenyl-trihydroxy-butyrolactone (p. 421), while the  $\Delta^2$ -lactone forms a dilactone, two molecules combining with each other (*Thiele*, Ann. 319, 196).  $\beta$ -Benzoyl-propionic acid condenses with aldehydes, the  $\alpha$ - or  $\beta$ - $CH_2$  group being attacked, according to the conditions. With acidic condensing agents the first, and with alkaline reagents the second reaction occurs. With phthalic anhydride it condenses to form 1-phthalidene-3-

phenyl-crotonolactone, 
$$C_6H_5\cdot C:CHC=C\cdot C_6H_5$$
  

$$\begin{array}{c} O \quad \quad O \quad \quad O \\ | \quad \quad | \quad \quad | \\ O-CO-O \quad CO \end{array}$$
, m.p.  $263-264^\circ$  (*Borsche*, Ber. 47, 1108; 48, 966).

When reduced,  $\beta$ -benzoyl-propionic acid is converted into  $\gamma$ -phenyl-butyrolactone, and it reacts with phosphorus pentasulphide to give phenyl-hydroxy-thiophen (*Paal*, Ber. 19, 553). Cf. laevulinic acid, Vol. I, p. 477. It gives two isomeric oximes, m.p.  $129^\circ$  and  $92^\circ$  (*Dollfus*, Ber. 25, 1932).

$\alpha$ -Methyl- $\beta$ -benzoyl-propionic acid,  $C_6H_5COCH_2CH(CH_3)COOH$ , m.p.  $136^\circ$ , is obtained by condensing benzene with pyruvic anhydride by means of aluminium chloride.  $\gamma$ -Benzoyl-butyric acid,  $C_6H_5COCH_2CH_2CH_2COOH$ , m.p.  $126^\circ$ , is obtained from benzene and glutaryl chloride in the presence of aluminium chloride, and by the ketonic hydrolysis of  $\alpha$ -benzoyl-glutaric ester (p. 437) (*Fichter*, Ber. 31, 2001).

$\alpha$ -Phenyl-laevulinic acid,  $C_6H_5\cdot CH \begin{cases} COOH \\ CH_2\cdot CO\cdot CH_3 \end{cases}$ , m.p.  $126^\circ$ , is obtained from phenyl-aceto-succinic acid (*Weltner*, Ber. 17, 72; 18, 790).  $\beta$ -Benzyl-laevulinic acid,  $C_6H_5\cdot CH_2\cdot CH \begin{cases} CH_2\cdot COOH \\ CO\cdot CH_3 \end{cases}$ , m.p.  $98^\circ$ , is obtained from  $\beta$ -benzylidene-laevulinic acid (*Erdmann*, Ann. 254, 202); see benzylidene-angelic-lactone, p. 488.

$\beta$ -Phenyl- $\gamma$ -acetyl-butyric acid,  $C_6H_5CH \begin{cases} CH_2COOH \\ CH_2\cdot COCH_3 \end{cases}$ , m.p.  $83^\circ$ , is obtained by the action of acids or alkalis on phenyl-dihydroresorcinol (*Vorländer*, Ann. 294, 332). When its ester is condensed with sodium ethylate, phenyl-dihydroresorcinol is regenerated.

$\gamma$ -Anisyl- $\gamma$ -ketobutyric acid, m.p.  $146^\circ$ , is obtained from anisole and succinic anhydride in the presence of aluminium chloride. Free hydroxyphenyl- $\gamma$ -ketonic acids are obtained from  $\beta$ -(hydroxybenzoyl)- $\alpha$ -ethyl chlorides,  $HO\cdot Ar\cdot CO\cdot CH_2CH_2Cl$ , by the action of potassium cyanide, followed by hydrolysis (*Arch. Pharm.* 272, 313).

Phenyl- $\delta$ - and higher ketonic acids are obtained by condensing benzene with the ester chloride of dihydric acids, e.g., the chloride of adipic ester.  $\delta$ -Benzoyl-valeric acid,  $C_6H_5CO(CH_2)_4COOH$ , m.p.  $71^\circ$ ; semicarbazone, m.p.  $183^\circ$ ; ethyl ester, b.p.  $164^\circ$  (3 mm.) (*Grateau*, C.r. 191, 947; Ger. Pat. 521,458).

## 9. Phenyl-alcohol Ketonic Carboxylic Acids

C-Benzoyl-glycolic acid,  $C_6H_5CO\cdot CH(OH)COOH$ , m.p.  $125^\circ$  (*Baeyer*, Perkin, Ber. 16, 2133).

$\alpha$ -Acyl-phenyl-glycolic esters, such as methyl *p*-tolyl-acetyl-glycolate,  $CH_3\cdot C_6H_4C(OH)COCH_2\cdot COOCH_3$ , b.p.  $190^\circ$  (15 mm.), and methyl *p*-dimethylaminophenyl-acetyl-glycolate,  $(CH_3)_2NC_6H_4C(OH)(COCH_3)COOCH_3$ , m.p.  $81^\circ$ , etc., are obtained by the condensation of aromatic hydrocarbons and anilines with  $\alpha$ , $\beta$ -diketobutyric ester. They are readily decomposed, giving aromatic aldehydes.

**Ethyl phenacetyl lactate**,  $C_6H_5CH_2COCH_2CHOHCOOC_2H_5$ , b.p.  $145^\circ$  (6 mm.), is obtained from phenacetyl chloride and ethyl lactate by means of pyridine (*Sabeta*, Bull. 47, 436).

**Acetoxypheyl-pyruvic nitrile**,  $C_6H_5CH(OCOCH_3) \cdot CO \cdot CN$ , m.p.  $52.5^\circ$ , b.p.  $150^\circ$  (10 mm.), is obtained by heating acetyl-mandelyl chloride with silver cyanide

(*Anschütz*, Ann. 368, 77). An acid,  $C_6H_5CH(NHC_6H_5)C \begin{smallmatrix} OH \\ COOH \\ N:CHC_6H_5 \end{smallmatrix}$ , m.p.

$194^\circ$ , should be regarded as a derivative of **phenyl-hydroxypyruvic acid**; its nitrile has been obtained by condensing anilinophenyl-acetonitrile (p. 413) with benzaldehyde and potassium cyanide (*Miller*, Ber. 29, 1732; 31, 2701).

**$\gamma$ -Phenyl- $\gamma$ -keto- $\alpha$ -hydroxybutyric acid**,  $C_6H_5 \cdot CO \cdot CH_2CH(OH) \cdot COOH$ , m.p.  $125^\circ$ , is obtained from its trichloride, **chloral-acetophenone**,  $C_6H_5 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CCl_3$ , m.p.  $76^\circ$  (*Koenigs*, Ber. 25, 795).

When phenyl-acetoacetic ester and  $\alpha$ -propionyl-phenyl-acetic ester (see above) are brominated, products are formed which are derived from position isomeric phenyl-keto-hydroxy-butyric acids; viz.,  $\alpha$ -bromo- $\alpha$ -phenyl-acetoacetic ester,  $Ar \cdot CBr(C_6H_5)COOC_2H_5$ , and  $\alpha$ -propionyl-phenyl-bromacetic ester,  $CH_3CH_2COCBr(C_6H_5)COOC_2H_5$ ,  $\gamma$ -bromo- $\alpha$ -phenyl-acetoacetic ester,  $CH_2BrCOCH(C_6H_5)COOC_2H_5$ , and  $\alpha'$ -bromopropionyl-phenylacetic ester,  $CH_3CHBrCOCH(C_6H_5)COOC_2H_5$ . The two first named compounds, on distillation with steam, break down into carbon monoxide, hydrogen, bromide, and ethyl atropate and ethyl  $\beta$ -methylatropate, respectively. The third and fourth, on heating with

water, give the lactones,  $\alpha$ -phenyl-tetronic acid,  $CH_2 \cdot C(OH) : C(C_6H_5)COO$ , m.p.

$254^\circ$ , and  $\alpha$ -phenyl- $\gamma$ -methyl-tetronic acid,  $CH_3 \cdot CH \cdot C(OH) : C(C_6H_5)COO$ , m.p.  $178^\circ$  (*Dimroth*, Ber. 39, 3929).  $\gamma$ -Phenyl-tetronic acid,  $C_6H_5 \cdot$

$CH \cdot C(OH) : CH \cdot COO$ , m.p.  $128^\circ$ , is obtained from the reaction product of acetyl-mandelyl chloride and sodio-malonic ester by hydrolysis and loss of carbon dioxide (*Anschütz*, Ann. 368, 65).

## 10. Diketo-carboxylic Acids

**Benzoyl-glyoxylic acid**,  $C_6H_5CO \cdot CO \cdot COOH$ . *Methyl ester* +  $1 H_2O$ , m.p.  $65^\circ$ ; *isobutyl ester hydrate*, m.p.  $62-63^\circ$ . Its *ethyl ester* is an orange-yellow oil, b.p.  $150-153^\circ$  obtained by passing nitrogen trioxide into a mixture of benzoyl-acetic ester (p. 429) and acetic anhydride. It readily combines with water and alcohols, forming *colourless* hydrates and alcoholates (*Wahl*, Bull. 1, 461; 13, 332). With *o*-phenylene diamine, the aroyl-glyoxyl esters form *quinoxalines*, and with phenylhydrazine, *pyrazolone* derivatives. The  $\alpha$ -oxime and  $\alpha$ -phenylhydrazone of the ethyl ester have been obtained from benzoyl-acetic ester by the action of nitrous acid (*Baeyer*, Ber. 16, 2133) and diazonium chloride (Ber. 21, 2120). **Ethyl benzoyl-isonitrosoacetate**,  $C_6H_5 \cdot CO \cdot C(:NOH)COOC_2H_5$ , m.p.  $121^\circ$ , and **ethyl benzoyl- $\alpha$ -phenylhydrazone glyoxylate**,  $C_6H_5 \cdot CO \cdot C(:N \cdot NHC_6H_5)COOC_2H_5$ , m.p.  $65^\circ$ . When benzoyl-isonitrosoacetic ester is reduced, benzoyl-aminoacetic ester is formed, and when this is diazotised, **benzoyl-acetic ester**

diazo-anhydride,  $C_6H_5 \cdot C \begin{smallmatrix} O \\ COOR \cdot N \end{smallmatrix} \rangle N$ , is formed (*Wolff*, Ber. 36, 3612). **Methyl**

**anisoyl-glyoxylate**, b.p.  $185-192^\circ$  (10 mm.), is obtained from anisoyl-acetic ester by the action of oxides of nitrogen (*Wahl*, C.r. 155, 49).

**Quinisatinic acid**, *o*-aminobenzoyl-glyoxylic acid,  $NH_2[2]C_6H_4CO \cdot CO \cdot COOH$ , is obtained by oxidising  $\beta, \gamma$ -dihydroxy-carbostyryl with ferric chloride. Heated

to  $120^\circ$  it gives a lactam, **quinisatin**,  $C_6H_4 \begin{smallmatrix} [1] CO \cdot CO \\ [2] NH \cdot CO \end{smallmatrix}$ , m.p.  $255-260^\circ$  (*Baeyer*,

Ber. 17, 985).

**Benzoyl-pyruvic acid**,  $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot COOH$ , or  $C_6H_5CO \cdot CH : C(OH) \cdot COOH$  (*Mumm*, Ber. 43, 3335), m.p.  $157^\circ$ , is prepared from its ethyl ester, m.p.  $43^\circ$ , which is the condensation product of acetophenone and oxalic acid (*Bromme*,

Ber. 21, 1131). This ester is also obtained from sodio-hydroxyacetophenone by the following method:  $\alpha$ -Phenyl-isoxazole is treated with dimethyl sulphate. The reaction product is converted into benzoyl-pyruvic nitrile  $\alpha$ -methylimide (*Mumm, loc. cit.*). Ferric chloride gives a blood-red colour with an alcoholic solution of the ester. For benzoyl-pyruvic chloralide, see *Schiff*, Ber. 31, 1306. For ring-substituted esters of benzoyl-pyruvic acid, see *Kostanecki*, Ber. 34, 2477; *Bülow*, Ber. 36, 2695.

**Benzoyl-acetoacetic ester**,  $C_6H_5 \cdot CO \cdot CH \begin{matrix} \swarrow COOC_2H_5 \\ \searrow COCH_3 \end{matrix}$ , is obtained from benzoyl

chloride and sodio-acetoacetic ester. It hydrolyses to benzoyl-acetone, or to ethyl benzoyl-acetate (p. 429). For *o*-, *m*-, and *p*-nitrobenzoyl-acetoacetic esters, see *Gevekoht*, Ann. 221, 323; *Bülow*, Ber. 35, 933.

**Acetophenone-acetoacetic acid**,  $C_6H_5 \cdot CO \cdot CH_2CH \begin{matrix} \swarrow COOH \\ \searrow COCH_3 \end{matrix}$ , melts between

130° and 140°, with decomposition into acetophenone and carbon dioxide. Its ethyl ester is obtained from  $\omega$ -bromo-acetophenone and sodio-acetoacetic ester (*Paal*, Ber. 16, 2866). It readily gives a furane derivative, like acetophenone-acetone. With alcoholic potash it gives  $\gamma$ -phenyl- $\alpha$ -acetyl-crotonolactone (p. 487).

**$\delta$ -Phenacyl-laevalinic acid**,  $C_6H_5COCH_2CH_2COCH_2CH_2COOH$ , m.p. 116°, is obtained by decomposition of *furfural-acetophenone*,  $(C_6H_5O)CH:CHCOOC_2H_5$ . With ammonia it gives phenyl-pyrrole-propionic acid (*Kehrer*, Ber. 34, 1263).

## 11. Phenyl Paraffin Dicarboxylic Acids

Like the aliphatic saturated dicarboxylic acids, the phenyl paraffin dicarboxylic acids can be classified as derivatives of malonic, ethylene-succinic acids, etc.

**PHENYL-MALONIC ACIDS.** Phenyl-malonic acid,  $C_6H_5 \cdot CH(COOH)_2$ , melts at 152° with loss of carbon dioxide, and formation of phenylacetic acid. It is obtained from benzyl-magnesium chloride by the action of carbon dioxide, followed by a second treatment with an alkyl-magnesium halide and carbon dioxide. The product decomposes into phenyl-malonic acid and an alkyl halide (*Ivanov*, C. 1931, I, 2046). Its ester, b.p. 171° (14 mm.), is obtained from phenyl-oxalacetic ester by loss of carbon monoxide (*Wislicenus*, Ber. 27, 1091). **Dinitrophenyl-malonic ester**,  $(NO_2)_2C_6H_3CH(COOC_2H_5)_2$ , m.p. 51°, is obtained from sodio-malonic ester and bromo-dinitro-benzene (*Richter*, Ber. 21, 2472; *Jackson*, Ber. 22, 1252; Am. Ch. J. 12, 307; 14, 331).

**Phenyl-cyanoacetic acid**,  $C_6H_5CH(CN) \cdot COOH$ , m.p. 92°. Its ethyl ester, b.p. 275°, is obtained by the action of sodium and ethyl carbonate on benzyl cyanide. Its amide, m.p. 147°, gives phenyl-malonic nitrile,  $C_6H_5CH(CN)_2$ , m.p. 69°, b.p. 153° (21 mm.), with phosphorus pentachloride (*Hessler*, Am. Ch. J. 32, 119).

**2,4,6-Trinitrophenyl-malonic acid**,  $(NO_2)_3C_6H_2CH(COOH)_2$ , m.p. 161°. Its ester exists in two modifications, m.p. 58° and 64° (*Jackson*, Ber. 18, 3066; Am. Ch. J. 18, 133; 21, 418). Di- and tri-nitrophenyl-malonic esters form salts of an intense red-brown colour, possibly of a quinoid structure (*Hantzsch*, Ber. 42, 2126). **Bromo-thymoquinone-malonic ester**, m.p. 78°,  $C_6O_2Br(CH_3)(C_6H_7) \cdot CH(COOC_2H_5)_2$ , forms blue metallic salts (*Hoffmann*, Ber. 34, 1558).

**Benzyl-malonic acid**,  $\beta$ -phenyl-isosuccinic acid,  $C_6H_5 \cdot CH_2 \cdot CH(COOH)_2$ , m.p. 117°, is obtained from its ester, which is formed by the action of benzyl chloride on sodio-malonic ester, or by the reduction of benzylidene-malonic acid (p. 488) (*Claisen*, Ann. 218, 139), or from benzyl-oxalacetic ester by loss of carbon monoxide (p. 438).

*o*- and *p*-Nitrobenzyl-malonic esters (*Lellmann*, Ber. 20, 434). The *o*-acid condenses to *N*-hydroxy- $\alpha$ -indole-carboxylic acid under the influence of sodium hydroxide (*Reissert*, Ber. 29, 639). **Methylbenzyl-malonic acid** (*Conrad*, Ann. 204, 177).

**Ethyl  $\alpha$ -phenyl-ethyl-malonate**,  $C_6H_5(CH_2)CH \cdot CH(COOC_2H_5)_2$ , b.p. 230° (15 mm.), is obtained from benzylidene-malonic ester and methyl magnesium

iodide. The acid melts at 144°, with decomposition into  $\beta$ -phenyl-butyric acid and carbon dioxide (Kohler, Am. Ch. J. 34, 132).

**PHENYL-SUCCINIC ACID.** Phenyl-succinic acid, 
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \overset{*}{\text{CH}} \cdot \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{COOH} \end{array}, \text{ m.p.}$$

167°, is obtained from  $\omega$ -chlorostyrene,  $\text{C}_6\text{H}_5\text{CH}:\text{CHCl}$ , or from ethyl benzylidene-malonate, by the action of potassium cyanide (Bredt, Ann. 293, 338), from ethyl phenyl-aceto-succinate (p. 435), from phenyl-ethane-tricarboxylic acid (p. 438), from  $\alpha,\delta$ -diphenyl-laevulinic acid by decomposition, from ethyl cyanophenylacrylate with potassium cyanide, followed by hydrolysis (Baker, Lapworth, J. 127, 560; Org. Synth. 8, 88), and from cinnamic acid by the action of potassium cyanide and hydrolysis (Higginbotham, J. 121, 49). There are two forms of the anhydride, m.p. 53° and 150° (Wegscheider, Mo. 24, 413; Dehn, Proc. 1906, 283). Chloride, b.p. 151° (12 mm.). Dimethyl ester, m.p. 58°, b.p. 161° (12 mm.). The acid has been resolved by means of its brucine salts: m.p. 173–174°,  $[\alpha]_D = 173^\circ$ ; *d*-methyl ester, b.p. 161–162° (16 mm.); *d*-ethyl ester, b.p. 166° (13 mm.) (Wren, J. 109, 572).

*Ester acids:* By the partial esterification of phenyl-succinic acid, and also by the addition of methyl alcohol to its anhydride,  $\alpha$ -hydrogen- $\beta$ -methyl-phenyl-succinate,  $\text{C}_6\text{H}_5\text{CH}(\text{COOH}) \cdot \text{CH}_2\text{COOCH}_3$ , m.p. 92°, and  $\alpha$ -methyl- $\beta$ -hydrogen-phenylsuccinate,  $\text{C}_6\text{H}_5\text{CH}(\text{COOCH}_3)\text{CH}_2\text{COOH}$ , m.p. 103°, are formed simultaneously, the product containing about 75% of the former. The  $\alpha$ -methyl- $\beta$ -hydrogen acid is obtained in a pure state by the partial hydrolysis of the dimethyl ester, and the  $\beta$ -methyl- $\alpha$ -hydrogen-acid by the hydrolysis of methyl- $\beta$ -phenyl- $\beta$ -cyano-propionate,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{CH}_2\text{COOCH}_3$ , m.p. 55°. The constitution of the two acids is proved by the reactions of the hydrogen ester chlorides obtained from them by the action of phosphorus pentachloride. With benzene and aluminium chloride, the one from the  $\beta$ -methyl- $\alpha$ -hydrogen-acid gives desylacetic ester (*q.v.*), while the other, obtained from the  $\alpha$ -methyl- $\beta$ -hydrogen acid gives phenyl-phenacylacetic ester (*q.v.*) (Anschtütz, Ann. 354, 117).

**Phenyl-succinic- $\beta$ -amide- $\alpha$ -acid**,  $\text{C}_6\text{H}_5\text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{CONH}_2$ , m.p. 145°, is obtained from its anhydride by adding on ammonia, and the isomeric **phenyl-succinic- $\alpha$ -amide- $\beta$ -acid**,  $\text{C}_6\text{H}_5\text{CH}(\text{CONH}_2) \cdot \text{CH}_2\text{COOH}$ , m.p. 150°, from  $\beta$ -phenyl- $\beta$ -cyano-propionic acid (see above). ***o*-Hydroxyphenyl-succinic acid**, m.p. 150° (decomp.), is obtained by the action of potassium cyanide on coumarin (Bredt, Ann. 293, 363). **2,4-Dimethoxyphenyl-succinic anhydride**, m.p. 147°, is obtained from maleic anhydride and resorcinol dimethyl ether with aluminium chloride (Rice, Am. 53, 3153).

**Phenyl-methyl-succinic acids**, 
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{COOH} \\ | \\ \text{CH}_3 \cdot \text{CH} \cdot \text{COOH} \end{array},$$
 have been obtained in two

forms, m.p. 170° and 192° (Zelinsky, Ber. 24, 1876). For other phenyl-alkyl-succinic acids, see Upson, Am. 44, 181.

**Benzyl-succinic acid**, 
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{COOH} \end{array}, \text{ m.p. 161}^\circ,$$
 is obtained from the

reaction product of benzyl chloride and sodio-ethane-tri- or -tetra-carboxylic esters (Baeyer, Ber. 17, 449), or from phenyl-itaconic acid by reduction (Fittig, Ann. 256, 50). Anhydride, m.p. 102°.

**Phenyl-ethyl-succinic acid**,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}(\text{COOH})\text{CH}_2\text{COOH}$ , m.p. 136°, is obtained by reduction of styryl-succinic acid (p. 490) and by the action of potassium cyanide on hydrocinnamal-malonic acid (p. 489).

**PHENYL-GLUTARIC ACIDS.**  **$\alpha$ -Phenyl-glutaric acid**,  $\text{C}_6\text{H}_5\text{CH}(\text{COOH}) \cdot \text{CH}_2\text{CH}_2\text{COOH}$ , m.p. 83°, is obtained by the hydrolysis of either  $\text{C}_6\text{H}_5\text{CH}(\text{COOR})\text{CH}_2\text{CH}(\text{CH}_2\text{CO})\text{COOR}$  or  $\text{C}_6\text{H}_5\text{C}(\text{COOR})_2\text{CH}_2\text{CH}_2\text{COOR}$ . It very readily forms its *anhydride*, m.p. 95° (Fichter, Ber. 34, 4175).

**$\beta$ -Phenyl-glutaric acid**,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_2\text{COOH})_2$ , m.p. 142°, is prepared from cinnamic or benzylidene-malonic ester and malonic ester by means of sodium ethylate. The primary condensation products,  $\beta$ -phenyl-propane- $\alpha,\alpha'$ -tri- and -tetra-carboxylic esters, are hydrolysed. On nitration, the acid gives a mixture of *o*-, *m*-, and *p*-nitrophenyl-glutaric acids, m.p. 205°, 204°, and 240°. The *o*-nitro-acid, when reduced with stannous chloride and hydrochloric acid,

gives hydrocarbostyryl- $\gamma$ -acetic acid,  $C_6H_5$   $\left\langle \begin{array}{l} [1]CH(CH_2COOH)CH_2 \\ [2]NH \text{-----} CO \end{array} \right.$ , m.p. 183°.

Homologous and substituted  $\beta$ -phenyl-glutaric acids are readily obtained from the condensation products of substituted benzaldehydes with malonic ester and sodium ethylate (*Meerwein*, Ber. 40, 1586; Ann. 360, 344).  $\beta$ -Phenyl- $\alpha$ -methyl-glutaric acid, m.p. 125°, is obtained from the addition product of methyl-malonic- and benzylidene-malonic esters.

## 12. Phenyl-alcohol-dicarboxylic Acids

Compounds of this class can be prepared by the general method of condensing aromatic hydrocarbons, anilines, and phenols with mesoxalic ester or alloxan (Vol. I, pp. 617, 633), by means of concentrated sulphuric acid. On oxidation they readily give the corresponding phenyl-glyoxylic acids and aromatic aldehydes (p. 266) as degradation products (*Guyot*, C.r. 148, 719; 149, 788).

Methyl phenyl-tartronate,  $C_6H_5C(OH)(COOCH_3)_2$ , m.p. 67°, b.p. 165° (11 mm.). Methyl *p*-tolyl-tartronate, m.p. 72°. Methyl *p*-methoxy- and *p*-dimethylamino-phenyl-tartronates, m.p. 118° and 115°. Ethyl trinitrophenyl-tartronate,  $(NO_2)_3C_6H_2C(OH)(COOC_2H_5)_2$ , m.p. 117°, is obtained from ethyl trinitrophenyl-malonate (see above) by oxidation with nitric acid (*Jackson*, Am. Ch. J. 21, 418).

Benzyl-tartronic acid,  $C_6H_5CH_2C(OH)(COOH)_2$ , m.p. 143° with decomposition into  $\beta$ -phenyl-lactic acid (p. 414) and carbon dioxide. It is obtained by the action of caustic potash on benzyl-chloromalonic ester, the reaction product of benzyl chloride and sodio-chloromalonic ester (*Conrad*, Ann. 209, 243).  $\alpha$ -Anilino- and -phenylhydrazino-benzylmalonic and similar esters are formed as addition products when bases are added to benzylidene-malonic ester (*Goldstein*, Ber. 28, 1451; 29, 813).

$\beta$ -Methoxybenzyl-malonic acid,  $C_6H_5CH(OCH_3) \cdot CH(COOH)_2$ , melts at 115° with decomposition into methyl alcohol and benzylidene-malonic acid. It is obtained from the ester of the latter by the addition of sodium methylate (*Liebermann*, Ber. 27, 289).

$\alpha$ -Aminobenzyl-malonic acids,  $Ar \cdot CH(NRR')CH(COOH)_2$ , are obtained from aromatic aldehydes and malonic acid by the action of ammonia or primary or secondary amines. Most of them are unstable and apt to lose carbon dioxide, phenyl- $\beta$ -amino-propionic acids being formed, or they lose the base and give cinnamic acids (*Radonow*, Am. 51, 841, 847).

Dioxyindole- $\beta$ -carboxylic esters, 3-hydroxyindole-3-carboxylic esters,

$C_6H_4 \left\langle \begin{array}{l} C(OH)COOR \\ >CO \\ NR' \end{array} \right.$ , are obtained from alkyl mesoxalates (Vol. I, p. 617) by the action of primary or secondary aromatic amines (*Martinet*, Rev. mat. colorantes, 23, 53; C. 1919, III, 710).

PHENYL-MALIC ACIDS.  $\alpha$ -Phenyl- $\alpha$ -hydroxysuccinic acid,

$C_6H_5C(OH)COOH$ , m.p. 187°, is obtained from phenyl-succinic acid by the action of bromine, phosphorus, and water.  $\alpha$ -Phenyl- $\beta$ -hydroxysuccinic acid,  $C_6H_5 \cdot CH \cdot COOH$

$\left| \begin{array}{l} CH_2 \cdot COOH \\ CH(OH) \cdot COOH \end{array} \right.$ , m.p. 150-160°, is obtained from phenyl-formylacetic ester, hydrocyanic acid, and hydrochloric acid (*Alexander*, Ann. 258, 67).

$C_6H_5CH_2 \cdot CH \cdot COOH$  Benzyl-hydroxysuccinic acid,  $\left| \begin{array}{l} CH(OH) \cdot COOH \end{array} \right.$ , m.p. 155°, is obtained from chloral and benzyl-malonic acid, the condensation product being hydrolysed with caustic potash (*Doebner*, Ber. 38, 2737).

Phenyl-paraconic acid,  $C_6H_5 \cdot CH \cdot CH \cdot COOH$

$\left| \begin{array}{l} CH_2 \\ O \text{-----} CO \end{array} \right.$ , m.p. 109°, the lactone of phenyl-itamalic acid, is obtained by heating benzaldehyde with sodium succinate and acetic anhydride, and by the reduction of phenyl-bromo-paraconic acid, which is itself obtained from phenyl-itaconic acid (p. 490). The stereoisomeric iso-

**phenyl-paraconic acid**, m.p. 168°, is a by-product of the last reaction. With boiling alkali, phenyl-paraconic acid gives the salts of phenyl-itamalic acid. From their solutions phenyl-paraconic acid is precipitated. Both phenyl-paraconic and *iso*-phenyl-paraconic acids can be resolved by means of strychnine (*Fittig*, Ann. 256, 63; 330, 292; Ber. 33, 1294; *Krautz*, Ann. 321, 127). On distillation, phenyl-paraconic acid breaks down to carbon dioxide, phenyl-butyrolactone (p. 418), and styryl-acetic acid (p. 469), the last forming further  $\alpha$ -naphthol. With sodium or sodium ethylate, phenyl-paraconic ester gives phenyl-itaconic acid (p. 490). It is reduced by hydriodic acid to benzyl-succinic and phenyl-butyric acids (*Shields*, Ann. 288, 203).

*o*-, *m*-, and *p*-**Chlorophenyl-paraconic acids** are obtained by condensing the monochloro-benzaldehydes with sodium succinate. They give three chloro-naphthols (*Erdmann*, Ann. 247, 366). 3,4-**Dichlorophenyl-paraconic acid**, m.p. 138°, gives two dichloro-naphthols (*Armstrong*, Proc. 1895, 78).  $\alpha$ - and  $\beta$ -**Methylphenyl-paraconic acids** are obtained by condensing benzaldehyde and pyruvic acid, and give methyl- $\alpha$ -naphthols (*Fittig*, Ann. 255, 257).

**$\alpha$ -Phenyl- $\gamma$ -valerolactone-carboxylic acid**,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CO} \cdot \text{COOH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}$ , m.p. 167°,

is obtained by the reduction of phenyl-acetosuccinic ester (p. 438) (*Weltner*, Ber. 18, 791).  $\delta$ -**Phenyl- $\delta$ -valerolactone- $\gamma$ -carboxylic acid**, m.p. 161°, is obtained by the reduction of  $\alpha$ -benzoyl-glutaric acid (see below); on distillation it gives  $\beta$ -styryl-propionic acid (p. 470).

### 13. Phenyl-keto-dicarboxylic Acids

**Benzoyl-malonic ester**,  $\text{C}_6\text{H}_5\text{CO} \cdot \text{CH} \cdot (\text{COOC}_2\text{H}_5)_2$ , is obtained by the action of benzoyl chloride on ethyl sodio-malonate, and *o*-**nitrobenzoyl-malonic ester** is obtained in a similar manner from *o*-nitrobenzoyl chloride. On reduction, the nitro-ester gives quinoline derivatives (*Bischoff*, Ber. 22, 386; Ann. 239, 92).

**Methyl benzoyl-cyanoacetate**,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH} \begin{matrix} \text{COOCH}_3 \\ \text{CN} \end{matrix}$ , m.p. 74°, is obtained

from methyl cyanacetate (Vol. I, p. 544) and benzoyl chloride. Its ethyl ester, m.p. 41°, obtained from ethyl benzoyl-acetate, gives cyano-acetophenone on boiling with water (p. 430).

**Ethyl phenacetyl-malonate**,  $\text{C}_6\text{H}_5\text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{COOC}_2\text{H}_5)_2$ , obtained from phenacetyl chloride and sodio-malonic ester, condenses under the influence of concentrated sulphuric acid to naphtho-resorcinol-carboxylic ester (*q.v.*) (*Metzner*, Ann. 298, 374). **Ethyl  $\omega$ -benzoyl-isosuccinate**,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}(\text{COOC}_2\text{H}_5)_2$ , is obtained from  $\omega$ -bromo-acetophenone and sodio-malonic ester (*Kues*, Ber. 18, 3324). **Ethyl  $\alpha$ -benzoyl-glutarate**,  $\text{C}_6\text{H}_5\text{COCH}(\text{COOC}_2\text{H}_5) \cdot \text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5$ , b.p. 200-210° (12 mm.), is obtained from sodio-benzoylacetic and  $\beta$ -iodopropionic esters.

$\beta$ -**Benzoyl-glutaric acid**,  $\text{C}_6\text{H}_5\text{COCH}(\text{CH}_2\text{COOH})_2$ , m.p. 122°, slowly loses water when maintained at a high temperature, the dilactone,

$\text{C}_6\text{H}_5\text{C} \begin{matrix} \diagup \text{CH}_2 \cdot \text{COO} \\ \diagdown \text{CH}_2 \cdot \text{COO} \end{matrix}$ , m.p. 137°, being formed. This dilactone is also ob-

tained synthetically from benzoic anhydride and sodium tricarballylate at 135-140°, carbon dioxide and water being lost. It readily opens to form  $\beta$ -benzoyl-glutaric acid. It is reduced by sodium amalgam to phenyl-butyrolactone-acetic

acid,  $\text{C}_6\text{H}_5\text{CH} \cdot \text{CH}(\text{CH}_2\text{COOH})\text{CH}_2 \cdot \text{COO}$ , m.p. 114° (*Fittig*, Ann. 314, 58).

**Phenyl-oxalacetic ester**,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CO} \cdot \text{COOC}_2\text{H}_5$ , is obtained by condensing

oxalic and phenylacetic esters with sodium (*Wislicenus*, Ber. 20, 592); see phenyl-malonic acid, p. 434. **Phenyl-cyano-pyruvic ester**,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN})\text{CO} \cdot \text{COOC}_2\text{H}_5$ , is obtained from ethyl oxalate and benzyl cyanide in the presence of sodium (*Erlenmeyer*, Ann. 271, 172); see phenyl-pyruvic acid, p. 428.

Phenyl-acetosuccinic ester,  $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{COOR}$   
 $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{COOR}$ , is obtained from sodio-acetoacetic ester and phenyl-bromoacetic ester (*Weltner*, Ber. 17, 71), and benzyl-acetosuccinic ester,  $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{C}(\text{COOR})_2\cdot\text{CH}_2\text{COOR}$ , is obtained from sodio-acetosuccinic ester and benzyl chloride (*Conrad*, Ber. 11, 1058). Benzyl-oxaloacetic ester,  $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{CH}(\text{COOC}_2\text{H}_5)_2$ , is an oil, obtained from oxalic and hydrocinnamic esters in the presence of sodium ethylate (*Wislicenus*, Ber. 31, 554).

#### 14. Phenyl-hydroxy-keto-carboxylic Acids

Phenyl-keto-paraconic ester,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{O}-\text{CO}-\text{CO})\cdot\text{CHCOOC}_2\text{H}_5$ , see *Wislicenus*, Ber.

26, 2144.  $\alpha$ -Benzoyl- $\delta$ -chloro- $\gamma$ -valerolactone,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}(\text{CH}_2)_3\cdot\text{CH}_2\text{Cl}$ , m.p. 106°, obtained from sodio-benzoylacetic ester and epichlorhydrin, is decomposed by the action of alkalis, partly into benzoic acid and  $\gamma,\delta$ -dihydroxyvaleric acid, and partly down to carbon dioxide and benzoyl-butane-diol,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{OH}$ , m.p. 91°.

#### 15. Phenyl Paraffin Tricarboxylic Acids

Phenyl-carboxyl-succinic acid, phenyl-ethane-tricarboxylic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{COOH})_2$ . The ester of this acid is obtained from phenyl-chloroacetic ester and sodio-malonic ester (*Spiegel*, Ann. 219, 31). The acid is decomposed on heating into carbon dioxide and phenyl-succinic acid (*Alexander*, Ann. 259, 67).

Ethyl  $\alpha,\beta$ -dicyano- $\beta$ -phenyl-propionate,  $\text{C}_6\text{H}_5\text{CH}(\text{CN})\cdot\text{CH}(\text{CN})\cdot\text{COOC}_2\text{H}_5$ , m.p. 68°, is obtained by the condensation of mandelonitrile with sodio-cyanacetic ester (*Higson*, J. 89, 1455).

$\alpha$ -Phenyl-tricarballic acid,  $\text{C}_6\text{H}_5\text{CH}(\text{COOH})\cdot\text{CH}(\text{COOH})\text{CH}_2\text{COOH}$ , m.p. 110°, is obtained by hydrolysing the reaction product of phenyl-itaconic ester (p. 490) and potassium cyanide (*Hecht*, Mo. 24, 367).

Phenyl-butane-tricarboxylic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}_2\text{COOH}$   
 $\text{CH}(\text{COOH})\text{CH}_2\text{COOH}$ , *trans*-form +  $\frac{1}{2}\text{H}_2\text{O}$ , m.p. 195°; *cis*, m.p. 179°, is obtained from the condensation product of cinnamic, sodio-cyanacetic, and bromoacetic esters by hydrolysis and loss of carbon dioxide. Both acids give one and the same anhydride-acid, m.p. 135° (*Thorpe*, J. 75, 904). The same structure has been assigned to a tricarboxylic acid, m.p. 200° (decomp.), which is obtained from the addition product of succinic and cinnamic esters. Its properties, however, are quite different (*Stobbe*, Ann. 315, 219).

$\beta$ -Phenyl-pimelic- $\beta_1$ -acetic acid,  $\text{C}_6\text{H}_5\text{CH}\cdot\text{CH}_2\text{COOH}$   
 $\text{CH}_2\cdot\text{CH}(\text{CH}_2\text{COOH})_2$ , m.p. 142°, is obtained by condensing cinnamic aldehyde with three molecules of sodio-malonic ester and hydrolysing the product with concentrated hydrobromic acid (*Meerwein*, Ann. 360, 337).

#### 16. Phenyl-keto-tricarboxylic Acids

$\alpha$ - and  $\beta$ -Benzoyl-tricarballic acids,  $\text{C}_6\text{H}_5\text{COCH}(\text{COOH})\text{CH}(\text{COOH})\cdot\text{CH}_2\text{COOH}$ , and  $\text{C}_6\text{H}_5\text{COC}(\text{COOH})(\text{CH}_2\text{COOH})_2$ . The ester of the former is obtained from chloro-succinic and benzoyl-acetic esters, and that of the latter

from benzoyl-succinic and bromoacetic esters using sodium ethylate as condensing agent (*Emery*, *J. pr.* 53, 312).

### 17. Phenyl-polyketo-polycarboxylic acids

When benzaldehyde or its substitution products condense with acetoacetic esters and similar substances in the presence of aliphatic amines, *polyketo-polycarboxylic acids* of the aromatic series are formed. A number of these show interesting isomerism and are capable of further condensation. How far, however, these compounds can still be supposed to contain open aliphatic chains, or how far they should be regarded as cyclic keto-hydroxy-carboxylic acids of the hydroaromatic series is an open question (*Rabe*, *Ann.* 323, 83; 332, 22).

**Benzylidene bis-acetoacetic ester**,  $C_6H_5CH[CH(COCH_3)COOC_2H_5]_2(?)$ , is obtained by condensing benzaldehyde with two molecules of acetoacetic ester, or by condensing benzylidene-acetoacetic ester with one molecule of acetoacetic ester, using piperidine as condensing agent. It exists in three stereoisomeric forms,  $\beta_1$  m.p. 150°,  $\beta_2$  m.p. 154°, and  $\beta_3$  m.p. 108°, which can be converted, by means of their sodium salts, into the corresponding keto-enol forms:  $\alpha_1$  m.p. 61°,  $\alpha_2$ , a liquid, and  $\alpha_3$  m.p. 65–67°. It condenses very readily with loss of water and formation of a cyclohexenone derivative (*Rabe*, *Ann.* 313, 129).

### APPENDIX

From the phenyl-polyalcohols and their oxidation products, a number of compounds are derived which contain, in addition to an aliphatic side-chain, one or more groups, usually carboxyl groups, attached to the benzene ring. The majority of these compounds are benzene *o*-derivatives, *e.g.*, *o*-phenylene-derivatives. Some have been prepared starting with phthalic acid, and others are oxidation products of derivatives of *o*-condensed hydrocarbons, such as indene and naphthalene. A number of these compounds will be referred to here; some of them, related to the dicarboxylic acids, have been dealt with in a preceding section (p. 393). In this latter group, one carboxyl group is attached to the ring and the other is in the side-chain.

### 18. Phenylene-hydroxy-dicarboxylic Acids

***o*-Carboxy-mandelic acid**,  $COOH[2]C_6H_4CH(OH)COOH$ , readily loses water with the formation of a lactone-carboxylic acid, *viz.*, **phthalide-carboxylic acid**,

$C_6H_4 \begin{array}{c} \text{CH}-COOH \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{array}$ , m.p. 151°, which decomposes at 180° to phthalide and carbon dioxide. It is obtained from *o*-carboxyphenyl-glyoxylic acid by reduction (*Scherks*, *Ber.* 18, 382; *Graebe*, *Ber.* 31, 373). It can also be obtained from ***ω*-dibromo-acetophenone-*o*-carboxylic acid**,  $HOCC_6H_4COCHBr_2$ , m.p. 132°, by boiling with water (*Gabriel*, *Ber.* 40, 71); from tetrachloro-hydrindone by the action of alkali; from *o*-phthalaldehydic acid by the action of potassium cyanide (*Seekles*, *Rec.* 43, 329); and from homophthalic anhydride by oxidation with permanganate (*Stevens*, *J.* 1928, 2827). Substituted phthalide-carboxylic acids, such as 5-methoxy-, 3,5-dimethoxy-, and 3,4,5-trimethoxy-phthalide-carboxylic acids have been obtained from substituted benzoic esters and chloral hydrate, with sulphuric acid as condensing agent; *trichloromethyl-phthalides* are formed, and these are decomposed by means of alkali (*Alimchandani*, *J.* 117, 964; *Fritsch*, *Ann.* 296, 344).

**Acetonyl-phthalide**,  $C_6H_4 \begin{array}{c} \text{CH}-CH_2COCH_3 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{array}$ , m.p. 68°, is obtained from acetone

and phthalaldehydic acid. **Phthalide-acetic acid**,  $C_6H_4 \begin{array}{c} \text{CH}-CH_2COOH \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{array}$ , m.p.

150°, is obtained from phthalyl-acetic acid (p. 491) by reduction (*Gabriel*, *Ber.* 10, 1558, 2200). **Meconine-acetic acid**,  $(CH_3O)_2[5,6]C_6H_2 \begin{array}{c} [1]CH-CH_2COOH \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \\ [2] \end{array}$ , m.p. 165–167°, is obtained from opianic and malonic acids, acetic acid and sodium



acetate, or ammonia, being used as condensing agents (*Liebermann*, Ber. 19, 2295).

**Dihydro-isocoumarin-carboxylic acid**,  $C_6H_4 \begin{matrix} [1]CH_2 \cdot CH \cdot COOH \\ [2]CO \end{matrix}$ , m.p. 153°, is isomeric with phthalide-acetic acid. It is formed in the oxidation of dihydro-naphthol with permanganate (*Bamberger*, Ber. 26, 1841).

**Phthalide-propionic acid**,  $C_6H_4 \begin{matrix} [1]CH-CH_2CH_2COOH \\ [2]CO \end{matrix}$ , m.p. 140°, is obtained in the reduction of phthalyl-propionic acid (*Gabriel*, Ber. 11, 1681).

***o*-Phenylene-acetic-glycol-lactonic acid**,  $C_6H_4 \begin{matrix} [1]CH(COOH) \cdot O \\ [2]CH_2- \end{matrix} \begin{matrix} O \\ CO \end{matrix} + 1\frac{1}{2} H_2O$ , m.p. 85°, is obtained from phenylene-diacetic acid by the action of bromine, phosphorus, and water (*Schad*, Ber. 26, 223).

***o*-Carboxyphenyl-glycerolic lactonic acid**,  $C_6H_4 \begin{matrix} [1]CH(OH)CHCOOH \\ [2]CO- \end{matrix} \begin{matrix} O \\ O \end{matrix}$ , m.p. 202°, is obtained from  $\beta$ -naphthoquinone by oxidation with sodium hypochlorite. When heated with hydrochloric acid, the lactonic acid loses water and forms *o*-carboxy- $\alpha$ -hydroxycinnamic lactone (*Bamberger*, Ber. 25, 892).

### 19a. Phenylene-monoketo-dicarboxylic Acids

***o*-Carboxyphenyl-glyoxylic acid, phthalonic acid**, m.p. 144°, is an oxidation product of *o*-hydrindene-carboxylic acid, naphthalene,  $\alpha$ -naphthol,  $\beta$ -naphthol, and  $\beta$ -phenyl-naphthalene-hydroxyquinone, when these substances are oxidised with permanganate (*Græbe*, Ber. 31, 369; *Zincke*, Ann. 240, 142). On reduction it gives *o*-carboxy-mandelic (see above) and later, homophthalic acids (p. 393). When heated by itself it gives phthalic anhydride, phthalaldehydic acid, and biphtalyl. Its anhydride is obtained by the action of acetic anhydride, m.p., 186° (*Kuroda*, J. 1923, 2094). When heated with sodium bisulphite, phthalaldehydic acid is obtained. For its esters and hydrogen esters see C. 1904, I, 514.

**Trichloroacetyl-benzoic acid**,  $C_6H_4 \begin{matrix} [1]COCCl_3 \\ [2]COOH \end{matrix}$ , m.p. 144°, and **tribromoacetyl-benzoic acid**, m.p. 160°, are obtained by the action of chlorine and bromine on phthalyl-acetic acid in glacial acetic acid (*Gabriel*, Ber. 10, 1556).

***o*-Carboxybenzoyl-acetic acid**,  $C_6H_4 \begin{matrix} [1]CO \cdot CH_2COOH \\ [2]COOH \end{matrix}$ , m.p. 90° with decomposition into acetophenone-*o*-carboxylic acid (p. 382) and carbon dioxide, is obtained by dissolving phthalyl-acetic acid in an excess of cold caustic soda and precipitating with an acid (*Gabriel*, Ber. 10, 1553).  **$\omega$ -Cyanoacetophenone-*o*-carboxylic acid**, m.p. 136° (*Müller*, C.r. 116, 760).

**Benzoyl-cyanoacetic ester-*o*-carboxylic acid**,  $COOH[2]C_6H_4COCH \begin{matrix} COOC_2H_5 \\ CN \end{matrix}$ , m.p. 121°, is obtained by the action of caustic soda on phthalyl-cyanoacetic ester. ***o*-Carboxybenzoylpropionic acid**,  $COOH[2]C_6H_4CO \cdot CH_2CH_2COOH$ , m.p.

137°. The corresponding dilactone,  $O \cdot COC_6H_4CH_2CH_2CO \cdot O$ , is obtained by heating succinic and phthalic anhydrides with sodium acetate (*Gabriel*, Ber. 11, 1680; *Roser*, Ber. 18, 3119).

### 19b. Phenylene-diketo-dicarboxylic Acids

The three phthalyl cyanides,  $C_6H_4(COON)^2$ , are obtained by a process similar to the *Claisen* synthesis of benzoyl cyanide; the three phthalyl chlorides and mercuric cyanide are boiled in acetone or heated in a sealed tube (*Blackstock*, Am. 34, 1080). These cyanides are brown powders, soluble in alkalis, ammonia, and

alcohol. At about 300°, they turn syrupy and decompose. They are hydrolysed with difficulty.

*m*-Xylylene-diacetoacetic ester,  $C_6H_4[1,3][CH_2 \cdot CH(COCH_3)COOR]_2$ , is obtained from *m*-xylylene bromide and sodio-acetoacetic ester (*Ephraim*, Ber. 34, 2790).

## 20. tri- and tetra-Carboxylic Acids

**Benzyl-malono-*o*-carboxylic acid**, *o*-carboxybenzyl-malonic acid,

$C_6H_4 \begin{matrix} \diagup CH_2CH(COOH)_2 \\ \diagdown COOH \end{matrix}$ , decomposes at 190° into hydrocinnamic-*o*-carboxylic acid and carbon dioxide. Its diethyl ester is obtained by reduction of phthalyl-malonic ester (*Wislicenus*, Ann. 242, 27).

**5-Carboxy-homophthalic acid**,  $COOH[5]C_6H_3[2]COOH[1]CH_2COOH$ , m.p. 220° (decomp.), is obtained from 5-nitro-homophthalic acid through the 5-amino- and 5-cyano-acids. Trimethyl ester, m.p. 95° (*Borsche*, Ber. 67, 678).

**Tetraethyl *o*-, *m*-, and *p*-xylylene-dimalonates**,  $C_6H_4[CH_2CH(COOC_2H_5)_2]_2$ , are the reduction products of the three **tetraethyl xylylene-dichloromalonates**,  $C_6H_4[CH_2CCl(COOC_2H_5)_2]_2$ , which, in their turn, are obtained from the  $\omega$ -xylylene dibromides and sodio-chloromalonate (*Kipping*, Ber. 21, 31). When heated, the xylylene-dimalonic acids decompose into phenylene-dipropionic acids and carbon dioxide.

## 21. Hydroxy-tri-, tetra-, and penta-Carboxylic Acids

**Phthalyl-diacetic acid**,  $C_6H_4 \begin{matrix} \diagup C[CH_2COOH]_2 \\ \diagdown COO \end{matrix}$ , m.p. 158°, is obtained from phthalyl-dimalonic acid,  $C_6H_4 \begin{matrix} \diagup C[CH(COOH)_2]_2 \\ \diagdown COO \end{matrix}$  (*Wislicenus*, Ann. 242, 80; *Scheiber*, Ann. 389, 121).

**Phthalide-tricarboxylic acid**,  $(COOH)_2C_6H_2 \begin{matrix} \diagup CH-COOH \\ \diagdown O \\ CO \end{matrix}$ , is obtained by the condensation of pyruvic and diacetyl-glyoxylic acid,  $(CH_3COO)_2CH \cdot COOH$ , in the presence of alkalis, by a process similar to the formation of uvitic and alkyl-isophthalic acids (p. 391). It loses water simply on boiling in water, *vic*-phthalide-dicarboxylic acid,  $C_6H_2 \begin{matrix} \diagup CH_2 \\ \diagdown CO \end{matrix} O$ , being formed. This gives mellophanic acid on oxidation (*Doehner*, Ann. 311, 132).

## 22. Keto-tricarboxylic Acids

**2,6-Dicarboxyphenyl-glyoxylic acid**,  $(COOH)_2[2,6]C_6H_3CO \cdot COOH$ , m.p. 238°, is obtained by oxidation of naphthalic acid with permanganate (*Grache*, Ber. 26, 1798). By reduction with hydriodic acid and phosphorus it is converted into 2-methyl-isophthalic acid (p. 391), and on heating it gives 2-aldehyde-isophthalic acid. Further oxidation gives hemimellitic acid.

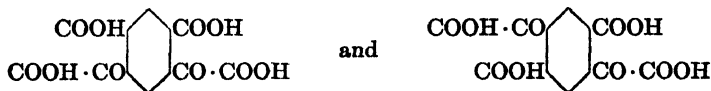
**Iregenone-dicarboxylic and -tricarboxylic acids**,

$CH_3[4]C_6H_3 \begin{matrix} \diagup [1]C(CH_3)_2COOH \\ \diagdown [2]CO \cdot COOH \end{matrix}$  and  $COOH[4]C_6H_3 \begin{matrix} \diagup [1]C(CH_3)_2COOH \\ \diagdown [2]CO \cdot COOH \end{matrix}$  (*Tiemann*, Ber. 26, 2684).

## 23. Diketo-tetracarboxylic Acids

When octahydro-anthracene is oxidised with alkaline permanganate, two isomeric **diphthalonic acids**, which have not yet been separated, are formed. On

further oxidation with acidified permanganate they give the two pyromellitic acids (p. 396). Their formulae are



(*Braun*, Ber. 57, 681).

## 10. MONONUCLEAR AROMATIC COMPOUNDS WITH UNSATURATED SIDE-CHAINS

So far we have dealt with benzene derivatives containing saturated side-chains. In the following section, compounds with unsaturated side-chains will be dealt with. Examples of such compounds are:

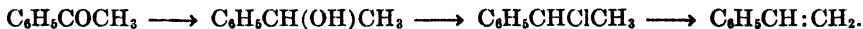
|                                 |                                                                                 |
|---------------------------------|---------------------------------------------------------------------------------|
| Phenyl-ethylene, styrene.....   | $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}_2$ .                          |
| Cinnamyl alcohol (styrone)..... | $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2\text{OH}$ . |
| Cinnamic aldehyde.....          | $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CHO}$ .           |
| Cinnamic acid.....              | $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{COOH}$ .          |
| Phenyl-acetylene.....           | $\text{C}_6\text{H}_5 \cdot \text{C} : \text{CH}$ .                             |
| Phenyl-propargyl alcohol.....   | $\text{C}_6\text{H}_5 \cdot \text{C} : \text{C} \cdot \text{CH}_2\text{OH}$ .   |
| Phenyl-propargaldehyde.....     | $\text{C}_6\text{H}_5 \cdot \text{C} : \text{C} \cdot \text{CHO}$ .             |
| Phenyl-propionic acid.....      | $\text{C}_6\text{H}_5 \cdot \text{C} : \text{C} \cdot \text{COOH}$ .            |

Like the unsaturated aliphatic compounds, they can readily be converted into saturated compounds by addition reactions of many types. Many such reactions have already been mentioned.

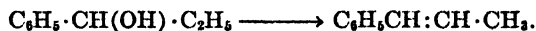
### Ia. Olefine-benzenes

The best starting materials for the preparation of these compounds, in which the olefine double bond is vicinal to the benzene ring, are sec.- and tert.-phenyl-alkyl-carbinols. These are readily prepared from synthetic acyl-benzenes (p. 281) by reduction, or by the action of magnesium-alkyl iodides. The primary alcohols also readily give olefine-benzenes on treatment with potassium carbonate or caustic potash.

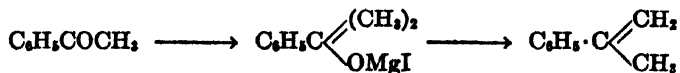
The carbinols may be treated as follows: (1) they may be acted upon by hydrogen chloride at  $0^\circ$ , when they are converted into chlorides. These lose hydrogen chloride when heated with pyridine (*Klages*, Ber. 35, 2245):



(2) Catalytic dehydration of the carbinols at  $290\text{--}300^\circ$  in the presence of alumina gives the olefine-benzenes directly:



(3) When acyl-benzenes or esters of benzene-carboxylic acids are combined with magnesium alkyl iodides, addition products are formed which decompose simply on heating with an excess of alkyl-magnesium iodide, or on treatment with dilute sulphuric acid or ammonia, with the formation of olefine-benzenes (*Klages*, Ber. 35, 2633, 3506):



(4) Benzene hydrocarbons with side-chains containing at least two carbon atoms (ethyl, *n*-propyl-benzene, *etc.*) are catalytically dehydrogenated at 650–700° (Br. Pat. 351,310; cf. Br. Pat. 340,587, Fr. Pat. 693,876).

$\Delta^1$ -,  $\Delta^2$ -, and  $\Delta^3$ -Olefine-benzenes are distinguished according to the position of the double bond with respect to the benzene ring. The  $\Delta^1$ -compounds differ from the  $\Delta^2$ - and  $\Delta^3$ -styrenes by having a higher density, a higher b.p., and an abnormally high molecular refraction, and a lower heat of combustion. The former, but not the latter, are readily reduced to alkyl-benzenes by means of sodium and alcohol (*Klages*, Ber. **36**, 1628, 3584; **37**, 2301; *Aunvers*, Ber. **62**, 693; Ann. **373**, 288).

On heating with alcoholic potash the  $\Delta^2$ -compounds rearrange into the isomeric  $\Delta^1$ -styrenes. This reaction appears to be reversible to a slight extent (*Agejeva*, C. **1905**, II, 1017).

**Styrene**, *phenyl-ethylene*, or *vinyl-benzene*,  $C_6H_5\cdot CH:CH_2$ , b.p. 144°, density 0.925 gm. per c.c., occurs to the extent of 1–5% in storax, from which it is recovered by steam distillation. It also occurs in coal-tar, where it comes over with crude xylene (*Kraemer*, Ber. **23**, 3169, 3269), and in the oils which condense from carburetted water gas (U. S. Pat. 1,640,975). It is obtained: (1) from  $\alpha$ -chloroethyl benzene on heating with pyridine at 130° (*Klages*, Ber. **36**, 1632), or from  $\alpha$ -bromoethyl-benzene by the action of alcoholic potash; (2) from  $\alpha$ -bromo-hydrocinnamic acid (p. 418), which, on heating with an aqueous solution of sodium carbonate decomposes smoothly into carbon dioxide, hydrobromic acid, and styrene; (3) from cinnamic acid, on heating with lime, or with water to 200°, or by pyrolysis of the vapour in a platinum tube at 150°; (4) from phenyl-acetylene by partial reduction with zinc and acetic acid, or sodium and methyl alcohol; (5) by the thermal condensation of acetylene,  $C_2H_2$ ; (6) from vinyl bromide or acetylene with benzene under the action of aluminium chloride (*Anschütz*, Ann. **235**, 331); (7) from the phenyl-ethyl alcohols by heating with potassium carbonate or caustic potash (*Sabetay*, *Palfray*, Bull. **45**, 69; C.r. **193**, 941), or with *p*-toluene-sulphonic acid (*Vernimmen*, Belg. **33**, 96); (8) from ethyl-benzene by catalytic dehydrogenation.

Styrene is a mobile liquid, with a high refractivity, and a pleasant smell. On standing, especially in sunlight, it polymerises to meta-styrene  $(C_8H_8)_x$ , which behaves like a saturated compound towards permanganate, and reverts to styrene when distilled. Quinone and aromatic nitro-compounds inhibit polymerisation to a large extent. For the mechanism of the polymerisation, see *Stobbe*, Ann. **371**, 259; **409**, 1. Polystyrene is largely used in the plastics industry.

**Reactions.**—On heating styrene with sodium and alcohol, ethyl-benzene is produced. With hydrogen chloride or bromide, it gives  $\alpha$ -halogenoethyl-benzene (*Schramm*, Ber. **26**, 1709). With chlorine or bromine, styrene gives  $\alpha,\beta$ -dihalogeno-ethyl-benzene (p. 401). Styrene combines with diazomethane to give 3-phenyl-pyrazoline (*Oliveri-Mandala*, Gazz. **40**, I, 117). It is oxidised by chromic or nitric acids to benzoic acid. With xylene and sulphuric acid, it forms  $\beta$ -phenyl- $\alpha$ -tolyl-propane, and with phenol, hydroxy-diphenyl-ethane (*Koenigs*, Ber. **24**, 3889). With nitrous acid, styrene- $\psi$ -nitrosite,  $[C_6H_5CH(NO)CH_2(NO_2)]_2$ , is formed; this compound isomerises to  $\omega$ -nitraceto-phenoxime,  $C_6H_5C(NO)CH_2NO_2$ , on boiling with alcohol, and with aniline and alkalis loses hyponitrous acid, and decomposes (*Wieland*, Ber. **36**, 2558). Styrene adds on diphenyl-keten (*q.v.*) with the formation of 2,2,3-triphenyl-cyclobutanone (Vol. II, p. 37) (*Staudinger*, Helv. **7**, 8). With aniline in the presence of aniline hydrohalides at 220–260° it reacts with the formation of *N*-( $\alpha$ -phenylethyl)-aniline,

$C_6H_5NH \cdot CH(CH_3)C_6H_5$ . For addition products of styrene with hydrocarbons, see *Spilker*, Ber. 65, 1686.

### A. Styrenes Substituted in the Side-chain

By replacement of hydrogen atoms in the vinyl residue, two series of mono-substituted styrenes are obtained, which are distinguished as the  $\alpha$ - and  $\omega$ -substitution products:

$\alpha$ -bromo-styrene,  $C_6H_5CBr:CH_2$ ;  $\omega$ -bromo-styrene  $C_6H_5 \cdot CH:CHBr$ .

$\alpha$ -Halogeno-styrenes are formed when styrene dichloride or dibromide is heated alone, or with lime, or with alcoholic potash. They have a pungent, lachrymatory smell, mainly due to the fact that they oxidise in air to  $\omega$ -halogeno-acetophenones with migration of the halogen (*Dufraisse*, C.r. 172, 162). When heated with water to  $180^\circ$ , or with sulphuric acid, they form acetophenone (*Erlenmeyer*, Ber. 14, 323).  $\alpha$ -Chloro-styrene has been obtained from acetophenone-chloride (p. 283) by the action of alcoholic potash, and  $\alpha$ -bromo-styrene has been obtained from phenyl-acetylene by the action of hydrogen bromide.

$\omega$ -Chlorostyrene, b.p.  $199^\circ$ ;  $\omega$ -bromo-styrene,  $\alpha$ -form, m.p.  $6-7^\circ$ ,  $\beta$ -form, f.p.  $-8$  to  $-7^\circ$ ;  $\alpha$ -chlorostyrene, b.p.  $190^\circ$ ;  $\alpha$ -bromostyrene, b.p.  $71^\circ$  (7-8 mm.); m.p.  $-43^\circ$ .

The  $\alpha$ -form of  $\omega$ -bromostyrene, which has a hyacinth-like smell, is prepared by warming dibromo-hydrocinnamic acid with aqueous sodium carbonate, and the  $\beta$ -form, which has an empyreumatic odour, is obtained by the action of powdered sodium hydroxide on bromo-benzylidene-acetophenone (*Dufraisse*, C.r. 171, 960).

$\omega$ -Halogeno-styrenes are obtained, together with phenyl-acetaldehyde (p. 269) by heating  $\beta$ -phenyl- $\alpha$ -halogeno-lactic acids, or better, by boiling the dihalides of cinnamic acid (p. 420) with aqueous sodium carbonate (*Biltz*, Ann. 296, 266; *Nef*, Ann. 308, 267).  $\omega$ -Chloro-styrene is also obtained from  $\omega$ -dichloroethyl-benzene by the action of alcoholic potash, and  $\omega$ -bromo-styrene by reduction of tribromo-methyl-phenyl-carbinol acetate. When heated with water they form phenyl-acetaldehyde. See also phenyl-acetylene (p. 446), and phenyl-propionic acid (p. 478).

*sym*-Dichloro-styrene,  $C_6H_5 \cdot CCl:CHCl$ , b.p.  $221^\circ$ , is obtained from phenacyl chloride (p. 404) or from  $\omega$ -chloro-acetophenone by the action of phosphorus pentachloride. When heated with ammonia it gives *diphenyl-pyrazine* (*Kunckell*, Ber. 33, 2654; 35, 2294). *as*-Dichloro-styrene,  $C_6H_5CH:CCl_2$ , b.p.  $225^\circ$ , is among the products formed by the action of chloral on benzene in presence of aluminium chloride, and is obtained from phenyl-trichloroethane by the action of caustic potash, and from trichloro-methyl-phenyl-carbinol acetate (p. 411) by reduction with zinc (*Biltz*, Ann. 296, 263). Trichlorostyrene,  $C_6H_5CCl:CCl_2$ , b.p.  $235^\circ$ . Dibromo-styrene, b.p.  $253^\circ$  (*Kinnicut*, Am. Chem. J. 5, 383; *Nef*, Ann. 308, 273). Di-iodo-styrene, m.p.  $76^\circ$ , is obtained from phenyl-acetylene and iodine. Tri-iodo-styrene,  $C_6H_5Cl:Cl_2$ , m.p.  $108^\circ$ , is obtained from phenyl-iodo-acetylene and iodine in carbon disulphide (*Peratoner*, Gazz. 22, II, 65).

$\omega$ -Nitro-styrenes are usually formed by the condensation of benzaldehydes with nitromethane, sodium ethylate, aliphatic amines (*Knoevenagel*, Ber. 37, 4502), dry alcoholic potash, or ammonium acetate and acetic acid (*Rao*, Helv. 12, 581), being used as condensing agents. In the first case, sodium salts of nitro-alcohols,  $C_6H_5CH(OH)CH:NOONa$ , are formed as intermediate products. Most of them readily lose water and form  $\omega$ -nitro-styrenes. The nitrostyrenes are reduced by aluminium amalgam, or zinc dust and acetic acid to aryl-acetaldoximes,  $C_6H_5 \cdot CH_2CH:NOH$ . By catalytic reduction with platinum black or palladium, nitrostyrene is converted into two isomeric  $\alpha,\delta$ -dinitro- $\beta,\gamma$ -diphenyl-butan-2-ols, m.p.  $238^\circ$  and  $97-98^\circ$  (*Sonn*, Ber. 50, 1513). For the direct reduction of  $\omega$ -nitrostyrenes to  $\omega$ -phenyl-ethylamines by hydrogen under pressure in the presence of colloidal platinum, see *Skita*, Ber. 65, 424.

$\omega$ -Nitrostyrene,  $C_6H_5 \cdot CH:CHNO_2$ , m.p.  $58^\circ$ , yellow needles with a pungent smell, volatile with steam, is obtained by boiling styrene with fuming nitric acid; by condensing benzaldehyde with nitromethane (*Thiele*, Ber. 31, 1293; Ann. 325,

7; Worrall, *Org. Synth.* 9, 66); by the action of fuming nitric acid on styryl-acetic acid (*Erdmann*, *Ber.* 17, 413); or by the action of nitrogen peroxide on cinnamic acid, when a di-nitrosite,  $C_6H_5 \cdot C_2H_2(N_2O_4) \cdot COOH$ , is first formed, and then decomposed (*Gabriel*, *Ber.* 18, 2438; *Sommer*, *Ber.* 29, 357). It is decomposed by dilute sulphuric acid into carbon monoxide, benzaldehyde, and hydroxylamine. It combines with sodium ethylate and methylate to form sodium salts:  $C_6H_5CH(OR) \cdot CH:NOONa$ , from which carbon dioxide liberates *phenyl-methoxy-* and *phenyl-ethoxy-nitro-ethane*, pale-yellow oils, b.p.  $136^\circ$  and  $137^\circ$  (12 mm.) (*Meisenheimer*, *Ber.* 38, 466). *p*-Phenylene-bis-nitroethylene,  $C_6H_4(CH:CH \cdot NO_2)_2$ , is obtained from terephthalaldehyde (p. 374) by the action of nitromethane (*Thiele*, *Ber.* 32, 1295). For nitro-halogeno-styrenes, see *Pfeffer*, *Ber.* 47, 1755.

Phenyl-vinylamine,  $\omega$ -aminostyrene,  $C_6H_5CH:CHNH_2$ , is very unstable. It is obtained from  $\alpha$ -amino-cinnamic acid (p. 464) on heating (*Plochl*, *Ber.* 17, 1622) and from  $\omega$ -nitrostyrene (*Komppa*, *Ber.* 26, R 677).

### B. Styrenes Substituted in the Benzene Nucleus

*p*-Chlorostyrene,  $Cl[4]C_6H_4 \cdot CH:CH_2$ , b.p.  $33-35^\circ$  (0.4 mm.), and *p*-bromostyrene, b.p.  $88^\circ$  (13 mm.) are obtained from the corresponding halogeno-cinnamic acids (*Braun*, *Ber.* 66, 1467). *o*-, *m*-, and *p*-Nitrostyrenes,  $NO_2C_6H_4 \cdot CH:CH_2$ , m.p.  $13^\circ$ ,  $-5^\circ$ , and  $29^\circ$ , are obtained from the nitrophenyl-bromolactic acids (p. 420) by the action of a cold aqueous solution of sodium carbonate, or from the  $\beta$ -lactones of these acids by boiling with water (*Einhorn*, *Ber.* 16, 2213; *Prausnitz*, *Ber.* 17, 595). *m*-Amino-styrene, b.p.  $112-115^\circ$  (12 mm.). *m*-Azostyrene, m.p.  $38^\circ$  (*Komppa*, *Ber.* 26, R 677). *o*-Amino-styrene, b.p.  $97-98^\circ$  (8 mm.). *p*-Amino-styrene, m.p.  $23.5^\circ$ , b.p.  $98-100^\circ$  (4 mm.), is obtained by the action of caustic potash on *p*-amino-phenyl-ethyl alcohol (*Sabetyay*, *Bull.* 45, 842). A polymeric *p*-amino-styrene, m.p.  $81^\circ$ , has been obtained by heating *p*-amino-cinnamic acid, and is a by-product in the reduction of *p*-nitro-cinnamic acid (*Bernthsen*, *Ber.* 15, 1932).

### C. Styrenes Substituted Both in the Side-chain and the Nucleus

*o*- and *p*-Nitro-acetophenones give *o*- and *p*-nitro- $\alpha$ -chloro-styrenes,  $NO_2 \cdot C_6H_4CCl:CH_2$ , with phosphorus pentachloride. The *o*-compound is a liquid, and the *p*- has m.p.  $63^\circ$  (*Gevekoht*, *Ann.* 221, 329). *o*-Nitro- $\omega$ -chloro-styrene,  $NO_2 \cdot C_6H_4 \cdot CH:CHCl$ , m.p.  $58^\circ$ , is obtained from *o*-nitro-cinnamic acid by the action of hypochlorous acid (*Lipp*, *Ber.* 17, 1070). *o*-Amino-chloro-styrene, m.p.  $56^\circ$ , gives indole with sodium ethylate at  $170^\circ$ . See also *o*-hydroxy- $\omega$ -chloro-styrene (p. 449). *o*-, *m*-, and *p*- $\omega$ -Dinitro-styrenes, m.p.  $107^\circ$ ,  $125^\circ$ , and  $199^\circ$  (decomp.), see *Posner*, *Ber.* 31, 657, *Bouveau*, *C.r.* 135, 41.

### D. Homologous Olefine-benzenes

*o*-, *m*-, and *p*-Methyl-styrenes,  $CH_3C_6H_4CH:CH_2$ , b.p.  $160^\circ$ ,  $164^\circ$ , and  $60^\circ$  (12 mm.); 4-ethyl-styrene, b.p.  $86^\circ$  (20 mm.); 2,4,5- and 2,4,6-trimethyl-styrenes, m.p.  $118^\circ$ , b.p.  $213^\circ$ , and b.p.  $92^\circ$  (14 mm.), have been obtained chiefly by method (I) (p. 442) (*Klages*, *Ber.* 31, 1007; 35, 2245; 37, 924; *Schramm*, *Ber.* 24, 1332). For other olefines of the mesitylene series and dimethyl-styrenes, see above references and *Heller*, *C.r.* 155, 1581.

Propenyl-benzene,  $\omega$ -methyl-styrene, isosallyl-benzene,  $C_6H_5 \cdot CH:CHCH_3$ , b.p.  $63.5^\circ$  (13 mm.), has been obtained by the action of pyridine on  $\alpha$ -chloropropyl-benzene, by reduction of cinnamyl alcohol with hydriodic acid, and by the action of sodium on ammonium cinnamate (*Emde*, *Ber.* 44, 3224). It has also been obtained by the action of methyl magnesium iodide on  $\omega$ -bromostyrene, and from  $\omega$ -chloroallyl-benzene (*Bert*, *C.r.* 191, 454); also by exhaustive methylation of  $\gamma$ -phenyl-propylamine (*Senfter*, *Ber.* 27, 2309). It can be obtained from  $\alpha,\beta$ -chloro-bromo-propenyl-benzene,  $C_6H_5CCl:CBCH_3$ , a transformation product of bromo-propenyl-benzene,  $C_6H_5 \cdot COCHBrCH_3$ , by reduction with sodium in ether (*Kunckell*, *Ber.* 36, 3033). For other  $\omega$ -alkyl-styrenes obtained by the action of magnesium alkyl-halides on benzaldehyde, see *Reich*, *Helv.* 4, 242; and for those obtained by dehydration of  $\alpha$ -alkyl- $\alpha$ -phenyl-ethanols, see *Amagat*, *C.r.* 190, 1055. *p*-Bromo-propenyl-benzene, m.p.  $35^\circ$ , is obtained from *p*-bromo-

phenyl-magnesium bromide and propionaldehyde, the carbinol first formed being dehydrated with phosphorus pentoxide (*Quelet*, Bull. 45, 75).

**Allyl-benzene**,  $C_6H_5 \cdot CH_2 \cdot CH : CH_2$ , b.p.  $157^\circ$ , is obtained from benzene, allyl iodide, and zinc dust (*Fittig*, Ann. 172, 132), or from phenyl magnesium bromide and allyl bromide (*Tiffeneau*, C.r. 139, 481). ***p*-Bromo-allyl-benzene**, b.p.  $96^\circ$  (12 mm.), is formed by the interaction of *p*-dibromo-benzene with magnesium and allyl bromide, only one of the bromine atoms attached to the ring reacting (see p. 443) (*Quelet*, Bull. 45, 75).

The allyl-benzenes boil at higher temperatures and have higher refractive indices than the propenyl-benzenes. The same is true of the corresponding phenol-ethers (pp. 449 *et seq.*) (*Auwers*, Ber. 62, 696).

**Isopropenyl-benzene**,  $C_6H_5C(CH_3) : CH_2$ , b.p.  $162^\circ$ , is obtained by the action of excess methyl magnesium iodide on acetophenone or benzoic esters; from  $C_6H_5C(CH_3)_2OMgI$  by the action of ammonia (p. 442); from hydratropyl alcohol by the action of caustic potash, and by heating dimethyl-phenyl-carbinol with acetic anhydride (*Sabotay*, Bull. 45, 69); it is also obtained by the elimination of hydrogen chloride from  $\beta$ -chloro- $\beta$ -phenyl-propane by sodio-malonic ester (*Hoffman*, Am. 51, 2542). By heating  $\beta$ -alkyl-cinnamic acids with 50% sulphuric acid, **methopropenyl-**, **methobutenyl-**, and **methohexenyl-benzenes**, b.p.  $192^\circ$ ,  $199^\circ$ , and  $121^\circ$  (20 mm.), have also been prepared (*Johnson*, J. 1926, 2748). For the elimination of formaldehyde from isopropenyl-benzene, see *Tiffeneau*, Bull. [3], 27, 1066.  **$\alpha$ -Ethyl-styrene**,  $C_6H_5C(C_2H_5) : CH_2$ , b.p.  $180^\circ$ , is obtained by the action of caustic potash on  $\beta$ -ethyl- $\beta$ -phenyl-ethyl alcohol (*Sabotay*, Bull. 45, 69). For optically active **methopentenyl-benzene**, b.p.  $100-103^\circ$  (9 mm.),  $[\alpha]_D 50.3^\circ$ , see *Klages*, Ber. 37, 653.  **$\omega$ -Chloroallyl-benzene**,  $C_6H_5CH_2CH : CHCl$ , obtained by the action of phenyl-magnesium bromide on 1,3-dichloro-propene, gives alkyl-ethers of cinnamyl alcohol with alcohols and caustic potash (*Bert*, C.r. 191, 332).  **$\beta$ -Bromoallyl-benzene**,  $C_6H_5CH_2CBr : CH_2$ , m.p.  $-12.5^\circ$ , b.p.  $102^\circ$  (17 mm.), is obtained from phenyl magnesium bromide and 2,3-dibromo-propylene, and with alcohols and caustic potash gives *sym*-phenyl-methyl-acetylene (*Lespieau*, C.r. 171, 111).  **$\omega$ -Bromo-isopropenyl-benzene**,  $C_6H_5C(CH_3) : CHBr$ , b.p.  $106^\circ$  (9 mm.), is obtained from dibromo- $\beta$ -methyl-cinnamic acid, by the action of an aqueous solution of sodium carbonate. With alcoholic potash it gives phenyl-allylene, with migration of the phenyl group (p. 447) (*Tiffeneau*, Ann. ch. ph. [8], 10, 145).

**$\Delta^2$ -Butenyl-benzene**,  $C_6H_5CH_2CH : CHCH_3$ , b.p.  $176^\circ$ ,  $d_{15} 0.8857$ ,  $n_D 1.5109$ , is obtained by reduction and loss of water from benzyl-acetone, or from phenyl-butadiene by reduction with sodium and alcohol. When heated with alcoholic potash to  $180^\circ$ , it changes into the isomeric  **$\Delta^1$ -butenyl-benzene**,  $C_6H_5CH : CH \cdot CH_2 \cdot CH_3$ , b.p.  $189^\circ$ ,  $d_{16} 0.9124$ ,  $n_D 1.5414$ . The latter compound is also obtained from benzaldehyde and propyl-magnesium bromide, and from phenyl magnesium bromide and *n*-butyraldehyde. Unlike  $\Delta^2$ -butenyl-benzene, it can be reduced to *n*-butyl-benzene by sodium and alcohol (*Klages*, Ber. 37, 2310).  **$\Delta^1$ -Butenyl-benzene**,  $C_6H_5CH_2CH_2CH : CH_2$ , b.p.  $73-76^\circ$  (14 mm.), is obtained from benzyl magnesium chloride and allyl iodide (*André*, Bull. 9, 192) or by the action of sodium on a mixture of benzyl chloride and allyl iodide (*Rüher*, Ber. 44, 2391). On oxidation it gives hydrocinnamic acid.

**$\Delta^1$ -Isoamenyl-benzene**,  $C_6H_5CH : CH \cdot CH(CH_3)_2$ , b.p.  $207^\circ$ .  **$\Delta^2$ -Isoamenyl-benzene**,  $C_6H_5CH_2 \cdot CH : C(CH_3)_2$ , b.p.  $205^\circ$ , see *Klages*, Ber. 37, 2314. For unsaturated hydrocarbons of the general formula  $C_6H_5(CH_2)_nCH : CH_2$ , which are obtained by the action of magnesium and allyl bromide on  $\omega$ -halogeno-alkyl-benzenes, see *Braun*, Ber. 45, 1246; for other homologues of styrene, see U.S. Pats. 1,541,175 and 1,552,874/5, and *Auwers*, Ber. 62, 693.

## Ib. Acetylene-Benzenes

**Phenyl-acetylene**,  $C_6H_5C \equiv CH$ , b.p.  $141-142^\circ$ , is obtained: (1) from  $\alpha$ - or  $\omega$ -bromo-styrene (*Strauss*, Ann. 342, 221; *Hezzler*, Am. 44, 425); (2) by heating acetophenone-chloride or styrene-dibromide with alcoholic potash at  $130^\circ$ ; (3) from phenyl-propionic acid (p. 478) by heating the acid with water at  $120^\circ$ , or by distilling its barium or aniline salt (*Holleman*, Rec. 15, 157), or by distilling its copper salt in steam.

Phenyl-acetylene is a liquid with a faint smell. Like acetylene it gives pre-

precipitates with ammoniacal silver and cuprous chloride solutions: silver phenyl-acetylide,  $C_6H_5C:C\text{Ag}$ , is white (*Liebermann*, Ber. 25, 1096); copper phenyl-acetylide,  $C_6H_5C:CCu$ , is bright yellow. It dissolves in acetic acid with an orange-yellow colour, forming an oxidisable double salt,  $C_6H_5C:C\cdot Cu, CH_3\cdot COOCu$ , and diphenyl-butenine (*q.v.*) (*Strauss*, Ann. 342, 193). Sodium phenyl-acetylide,  $C_6H_5\cdot C:CNa$ , is obtained by the action of sodium on a solution of phenyl-acetylene in ether. It condenses with aldehydes and ketones to form phenyl-acetylene alcohols (p. 457), with formic ester to give phenyl-propargaldehyde (p. 461), with the esters or chlorides of homologous acids to give phenyl-acetylene ketones, with ethyl chlorocarbonate to give phenyl-propionic ester (p. 479), and with carbon dioxide to give phenyl-propionic acid. With aromatic mustard oils it forms *thio-analides*,  $C_6H_5C:C\cdot CS\cdot NH\cdot Ar$ ; *p*-toluidide, m.p. 111–113° (decomp.) (*Worrall*, Am. 39, 697). Phenyl-acetylene is converted into acetophenone by treatment with dilute sulphuric acid, and into styrene, with a little diphenyl-butadiene as a by-product, by boiling with acetic acid, or ethyl alcohol, and zinc dust (*Aronstein*, Ber. 22, 1184). With hydrogen bromide it gives  $\alpha$ -bromo-styrene (p. 444). For its gradual hydrogenation, see *Bourguet*, C.r. 189, 757.

**Phenyl-chloroacetylene**,  $C_6H_5C:CCl$ , b.p. 74° (14 mm.); **phenyl-bromo-acetylene**,  $C_6H_5C:CBr$ , b.p. 96° (15 mm.), and **phenyl-iodoacetylene**, b.p. 136° (22 mm.) are all converted into phenacyl halides (p. 404) by sulphuric acid (*Peratoner*, Gazz. 22, II, 94; *Nef*, Ann. 308, 292). Various aryl-chloro-acetylenes have been obtained from  $\alpha, \beta$ -dichloro-styrenes with alcoholic potash, while metallic sodium gives rise to *aryl-acetylenes* (*Kunckell*, Ber. 33, 2654, 3261). For  $\omega$ -bromo- and  $\omega$ -iodo-phenyl-alkynes, see *Grignard*, Ann. ch. [10], 5, 5. *o*- and *p*-**Nitrophenyl-acetylenes**,  $NO_2C_6H_4C:CH$ , m.p. 81° and 152°, are obtained by boiling *o*- and *p*-nitrophenyl-propionic acids with water. *m*-**Azoxyphenyl-acetylene**,  $N_2O[3](C_6H_4C:C)_2$ , pale rose-coloured crystals, m.p. 101–102°, is obtained from *m*-azoxyphenyl-propionic acid (p. 480) by heating with water in a sealed tube at 135° (*Reich*, Bull. 19, 146). *o*-**Aminophenyl-acetylene**,  $NH_2\cdot C_6H_4C:CH$ , is an oil, smelling like the indigo vat. It is obtained from *o*-aminophenyl-propionic acid, or from *o*-nitrophenyl-acetylene by reduction with powdered zinc and ammonia, or ferrous sulphate and caustic potash.

**TRUE ARYL-ACETYLENES**,  $Ar\cdot C:CH$ . *p*-**Tolyl-acetylene**, m.p. 23°, b.p. 53–56° (11–12 mm.), is obtained from the dichloride of methyl-*p*-tolyl ketone by the action of sodamide (*Willemart*, Bull. 45, 644).  $\gamma$ -**Phenyl-propine**, or **benzyl-acetylene**,  $C_6H_5CH_2C:CH$ , b.p. 68° (16 mm.), has been obtained from the  $\beta$ -isomer, *sym*-phenyl-methyl-acetylene (see below), which isomerises under the influence of sodamide (*Bourguet*, Ann. ch. [10], 3, 325) or from *as*-benzyl-bromo-ethylene,  $C_6H_5CH_2CBr:CH_2$ , by the same method. Like all true acetylenes it gives a silver compound,  $C_7H_7C:C\text{Ag} + AgNO_3$ . With sodamide, a red derivative is formed, not only the mobile H atom of the CH group, but also one of the hydrogens of the methylene group taking part in the reaction (*Bourguet*, C.r. 176, 751; 186, 1211).  $\delta$ -**Phenyl-butine**, **phenyl-ethyl-acetylene**,  $C_6H_5CH_2CH_2C:CH$ , b.p. 79–81° (12 mm.), has been obtained from the dibromide of  $\Delta^3$ -butenyl-benzene (p. 446) by the action of alcoholic potash (*André*, Bull. 9, 192). For other true acetylenes, see *Bert*, C.r. 181, 555.

*sym*-**Phenyl-methyl-acetylene**,  $\beta$ -**phenyl-propine**, **phenyl-allylene**,  $C_6H_5\cdot C:C\cdot CH_3$ , b.p. 185°, is obtained from phenyl-bromopropylene by the action of alcoholic potash, or from phenyl-acetylene, methyl iodide, and caustic potash (*Bourguet*, C.r. 192, 686). For bases of the general formula  $C_6H_5C:C\cdot CH_2\cdot NR_2$ , which are obtained from the aryl-acetylenes by the action of formaldehyde and secondary amines, see *Mannich*, Ber. 66, 418. *sym*-**Phenyl-ethyl-acetylene**, b.p. 201°, is obtained from sodio-phenyl-acetylene by the action of ethyl iodide, or from phenyl-iodo-acetylene by the action of zinc diethyl. *sym*-**Phenyl-butyl-acetylene**,  $C_6H_5C:CC_4H_9$ , b.p. 114–115° (14 mm.), is obtained from phenyl-acetylene and butyl benzene-sulphonate in vaseline at 110° (*Truchet*, Ann. ch. [10], 16, 309).

### 1c. Diolefine-benzenes

(A) *o*-, *m*-, and *p*-**DIVINYLBENZENES**,  $C_6H_5(CH:CH)_2$ , b.p. 78.5° (11 mm.), 52° (3 mm.), and m.p. 31°, are obtained by the action of quinoline on



the dibromohydrins of *o*-, *m*-, and *p*-di-(hydroxy-ethyl)-benzenes. *Tetra-bromides*, m.p. 71–74°, 64°, and 157° (indefinite) (*Lespieau*, C.r. 190, 683; 192, 1382). *p*-Dipropenyl-benzene,  $C_6H_4(CH:CHCH_3)_2$ , b.p. 123–125° (12 mm.), has been prepared by heating the carbinol (*q.v.*) with phosphorus pentoxide (*Quelet*, Bull. 45, 255), and *p*-diisopropenyl-benzene,  $C_6H_4[C(CH_3):CH_2]_2$ , m.p. 63.6–64°, is obtained similarly, but using potassium bisulphate in place of phosphorus pentoxide (*Bogert*, Am. 41, 1676).

(B) Phenyl-butadiene,  $C_6H_5CH:CH:CH:CH_2$ , m.p. 4.5°, b.p. 95° (18 mm.), is obtained: by the action of excess methyl magnesium iodide on cinnamic aldehyde (*Klages*, Ber. 37, 2310); by loss of carbon dioxide from cinnamylidene-malonic- or -acetic acids (p. 480), and from styryl-methyl-carbinol chloride,  $C_6H_5CH:CH:CHCl \cdot CH_2$ , by boiling with pyridine. It polymerises into the dimer on standing, and more rapidly at 150°, the compound produced boiling at 221° (17 mm.) (*Riiber*, Ber. 37, 2272; *Stobbe*, Ber. 45, 3496). Phenyl-butadiene is reduced by sodium and ethyl alcohol to  $\Delta^2$ -butenyl-benzene (p. 446). With bromine it gives a 1,4-dibromide,  $C_6H_5CHBrCH:CH:CH_2Br$ , m.p. 94°, and a tetrabromide,  $C_6H_5CHBrCHBr \cdot CHBr \cdot CH_2Br$ . The dibromide reacts with zinc methyl and ethyl to form dimethyl- and diethyl-butenyl-benzenes,  $C_6H_5CH(Alk)-CH:CHCH_2(Alk)$ . Phenyl-butadiene combines with diazo-acetic ester to form

styryl-cyclopropane-carboxylic ester,  $C_6H_5CH:CH \cdot CH \begin{matrix} \diagup CH \cdot COOR \\ | \\ CH_2 \end{matrix}$  (*von der*

*Heide*, Ber. 37, 2101). When  $\beta$ -styryl-acrylic (cinnamylidene-acetic) or cinnamylidene-malonic acid, is heated with baryta, phenyl-cyclobutene,  $C_6H_5-CH-CH_2-CH:CH$ , m.p. 25°, is formed, while the dimeric diphenyl-tricyclo-

octane is the chief product (*Klages*, Ber. 35, 2649; *Liebermann*, *Riiber*, Ber. 35, 2696; 36, 1404; *Döbner*, Ber. 40, 149).

Phenyl-methyl-butadiene,  $C_6H_5CH:CH \cdot C(CH_3):CH_2$ , b.p. 124° (32 mm.), and phenyl-methyl-pentadiene,  $C_6H_5CH:CH \cdot C(CH_3):CHCH_3$ , b.p. 133° (21 mm.), are obtained from benzylidene-acetone by the action of methyl magnesium iodide and ethyl magnesium iodide by method (3) (p. 442). Phenyl-pentadiene,  $C_6H_5CH:CH \cdot CH:CH \cdot CH_2$ , b.p. 116° (16 mm.), and phenyl-hexadiene,  $C_6H_5CH:CH:CH:CH:CH \cdot CH_2CH_3$ , b.p. 128° (16 mm.), are obtained from cinnamaldehyde with ethyl magnesium iodide and propyl magnesium iodide (*Klages*, Ber. 35, 2651; 40, 1768).

Trimethyl-phenyl-allene,  $C_6H_5(CH_3)C:C:C(CH_3)_2$ , b.p. 108° (20 mm.), is a liquid of high refractive index, possessing a lemon-like odour, obtained by the action of phenyl magnesium bromide on mesityl oxide. When oxidised with permanganate it gives acetophenone, and on reduction with sodium and alcohol it gives  $\Delta^2$ -hexenyl-benzene (*Klages*, Ber. 37, 2305).

## Id. Olefine-acetylene-benzenes

Compounds such as isopropenyl-phenyl-acetylene,  $C_6H_5C:C \cdot C(CH_3):CH_2$ , b.p. 88° (7 mm.), and isobutenyl-phenyl-acetylene,  $C_6H_5C:C \cdot C(CH_3):CH \cdot CH_3$ , b.p. 103° (9 mm.), have been prepared from phenyl-acetylene-alcohols by the removal of water by means of sulphuric acid or potassium bisulphate (*Favorski*, C. 1905, II, 1018, *et seq.*)

## Ie. Diacetylene-benzenes

*o*-, *m*- and *p*-Diethynyl-benzenes, phenylene-diacetylenes,  $C_6H_4(C \equiv CH)_2$ , b.p. 82° (14 mm.), m.p. –2.5° and 95°, are obtained from the tetrabromides of diolefine-benzenes (see above) by the action of alcoholic potash (*Lespieau*, C.r. 190, 683; 192, 1387).

## Iia. Olefine-phenols

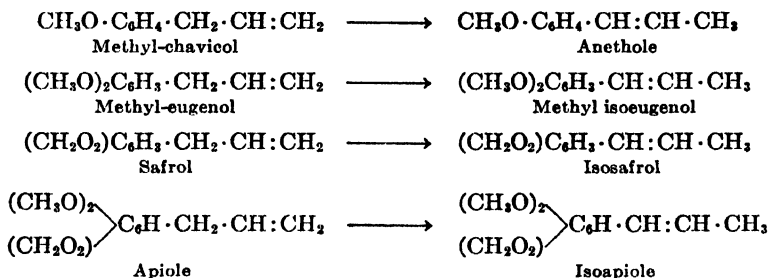
A number of compounds of this class occur in plants. Chavicol, estragol, anethole, eugenol, chavibetol, safrol, asarone, apiole, *etc.*, are

all phenolic derivatives of allyl-benzene and isoallyl- or propenyl-benzene. Some of them have been synthesised, the allyl compounds by means of the *Claisen reaction* described on p. 193, and the propenyl compounds from aldehydes by condensation with propionic acid and removal of carbon dioxide, or with ethyl magnesium bromide and removal of water, or from allyl compounds by rearrangement.

### 1. Olefine-monohydroxy-benzenes

*o*-Vinyl-phenol,  $\text{CH}_2\text{:CH}\cdot\text{C}_6\text{H}_4\text{OH}$ , m.p.  $29^\circ$ , b.p.  $108^\circ$  (15 mm.), a compound with a phenol-like smell, is obtained by slowly distilling *o*-coumaric acid (p. 473) in a vacuum (*Fries*, Ber. 41, 367), and from phenol by the action of ethylene oxide and sulphuric acid (*Smith*, Am. 53, 806). *m*-Vinyl-phenol, b.p.  $115^\circ$  (16 mm.), is obtained from *m*-aminostyrene (p. 445). *o*-, *m*- and *p*-Vinyl-anisoles,  $\text{CH}_2\text{:CH}\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3$ , b.p.  $83^\circ$  (11 mm.),  $90^\circ$  (14 mm.),  $91^\circ$  (13 mm.), are oils which readily polymerise. They have been obtained by method (1) (p. 442) from methoxy-acetophenones. The *o*- and *p*-derivatives have also been synthesized from methoxy-cinnamic acids (*Perkin*, Ber. 11, 515; *Klages*, Ber. 36, 3587). *o*-Hydroxy- $\omega$ -chlorostyrene,  $\text{HO[2]C}_6\text{H}_4\text{CH:CHCl}$ , m.p.  $54^\circ$ , obtained from *o*-amino- $\omega$ -chlorostyrene, gives coumarone when treated with caustic potash. *p*-Methoxy- $\omega$ -chlorostyrene,  $(\text{CH}_3\text{O})[4]\text{C}_6\text{H}_4\text{CH:CHCl}$ , m.p.  $34^\circ$ , is obtained from *p*-methoxy-cinnamic acid (p. 476) dissolved in aqueous potassium carbonate by the action of potassium hypochlorite (*Borsche*, Ber. 48, 452). The three hydroxy- $\omega$ -nitrostyrenes,  $\text{HO}\cdot\text{C}_6\text{H}_4\text{CH:CHNO}_2$ , have been obtained by similar methods to the  $\omega$ -nitro-styrenes (p. 444) from *o*- and *m*-hydroxy-aldehydes, and from the acylated *p*-hydroxy-aldehyde; m.p. *o*-  $133\text{--}134^\circ$ , *m*-  $132\text{--}133^\circ$ , *p*-  $165^\circ$  (*Remfry*, J. 99, 282). For *o*-thio- $\omega$ -chlorostyrene,  $\text{HS}\cdot\text{C}_6\text{H}_4\cdot\text{CH:CHCl}$ , see benzo-thiophene, Vol. IV.

**ALLYL- AND PROPENYL-PHENOLS.** A property common to all the allyl-phenols comprising this group is their isomerisation to propenyl compounds under the influence of hot alcoholic potash, powdered caustic potash or caustic soda, potassium phenate, etc.:



The change seems to be confined to allyl derivatives, since  $\beta$ -butenyl-*p*-anisole does not undergo a similar rearrangement into  $\alpha$ -butenyl-anisole (*Braun*, Ber. 56, 538). It is possibly connected with the ready migration of the allyl group in the phenol-allyl ethers (p. 193).

The propenyl derivatives differ from the allyl derivatives in having higher specific gravities, higher melting points, higher refractive indices, and lower heats of combustion (*Eykman*, Ber. 22, 2747; *Auwers*, Ber. 62, 696). Often, two geometrically isomeric forms exist (*Waterman*, Rec. 47, 1027). While the propenyl compounds are readily reduced by sodium and alcohol, the allyl compounds are not (*Klages*, Ber. 32, 1436). On catalytic hydrogenation under pressure, the unsaturated side-chain is first reduced at a temperature of about  $95^\circ$ , but the benzene ring is not affected until the temperature has been raised to  $185\text{--}190^\circ$  (*Ipatiev*, Ber. 46, 3589). By careful oxidation with permanganate, the allyl- and propenyl-phenols give phenol-glycols (p. 376) and phenol-glyoxylic acids (p. 422). On ozonisation, hydroxy-benzaldehydes and hydroxyphenyl-acetaldehydes are

formed (*Semmler*, Ber. 41, 2751). The propenyl compounds are oxidised by mercuric acetate, mercurous acetate being precipitated and glycols formed, while the allyl compounds merely form addition products, from which they are regenerated by acids, or by reduction (*Balbiano*, Ber. 36, 3577; 42, 1502; Gazz. 36, I, 237). Propenyl-phenols and their ethers are dimerised and polymerised even in the cold in the presence of mineral acids (*Puxeddu*, Gazz. 43, I, 128); concentrated formic acid produces the same effect on boiling. The allyl compounds are not affected by this treatment. When the iodohydrins of the propenyl compounds are treated with silver nitrate, or mercuric oxide, the aromatic residue migrates and aldehydes are formed. Thus anethole gives *p*-methoxy-hydratropaldehyde,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CHO}$  (p. 347). In the dibromides of the propenyl compounds, the bromine atom next to the phenyl group is mobile; unlike the allyl dibromides, they readily give ketones on treatment with two molecules of sodium methylate. Thus anethole dibromide gives *anisyl-ethyl ketone*, b.p.  $148^\circ$  (14 mm.) (see pp. 351, 400).

**Chavicol**, *p*-allyl-phenol,  $\text{CH}_2=\text{CH}\cdot\text{CH}_2[4]\text{C}_6\text{H}_4\text{OH}$ , m.p.  $-16^\circ$ , b.p.  $236^\circ$ ,  $d_{15}^{20}$  1.020, occurs in the essential oil of bay and in betel oil, from the leaves of *Chavica betle*. It has been synthesised by *Quelet* (Bull. 45, 255) by oxidising *p*-allyl-phenyl-magnesium bromide with oxygen. Its aqueous solution gives a blue colouration with a drop of ferric chloride.

**O-Methyl-chavicol**, *estragol*, b.p.  $215^\circ$ , has been detected in tarragon oil, in American turpentine, and in other essential oils (*Grimaux*, C.r. 117, 1089; *Hell*, Ber. 29, 344). It has been synthesised by *Triffeneau* from allyl bromide and *p*-methoxy-phenyl-magnesium bromide (C.r. 139, 481). Heated with alcoholic potash, it is converted into anethole.

**p-Anol**, *p*-propenyl-phenol,  $\text{CH}_3\cdot\text{CH}:\text{CH}[4]\text{C}_6\text{H}_4\text{OH}$ , m.p.  $93-94^\circ$ , has been obtained by heating anethole with caustic potash, or synthetically, from *p*-hydroxy-benzaldehyde by the action of excess ethyl magnesium bromide (*Behal*, Bull. 3, 301; *Landenburg*, Ann. supp. 8, 88) and by oxidation of *p*-propenyl-phenyl-magnesium bromide with oxygen (*Quelet*, Bull. 45, 255).

**Anethole**, *p*-propenyl-anisole,  $\text{CH}_3\cdot\text{CH}:\text{CH}[4]\text{C}_6\text{H}_4\text{OCH}_3$ , m.p.  $22^\circ$ , b.p.  $233^\circ$ , is found in anise oil, from the seed of *Pimpinella anisum*, in star anise oil from the seed of *Illicium verum*, in fennel oil from the fruit of *Anethum foeniculum*, and in tarragon oil; it is also obtained from methyl-chavicol (see above). Syntheses have been carried out by *Hell*, from anisaldehyde and ethyl-magnesium iodide (Ber. 37, 4188), and by *Perkin* and *Wallach* (Ber. 10, 1604; Ann. 357, 76), from  $\beta$ ,*p*-methoxyphenyl-methylacrylic acid by heating. This reaction establishes its constitution as a *p*-propenyl-anisole. When boiled with methyl alcoholic hydrogen chloride it dimerises to *iso-anethole*, b.p.  $205-210^\circ$  (0.7 mm.), the formula of which, deduced from its oxidation products, is probably  $\text{CH}_3\text{O}[4]\text{-C}_6\text{H}_4\text{CH}:\text{C}(\text{CH}_3)\cdot\text{C}(\text{C}_6\text{H}_5)\text{C}_6\text{H}_4[4']\text{OCH}_3$  (*Godall*, J. 1930, 2482). A dimeric anethole, m.p.  $132^\circ$ , possibly different from the preceding compound, is formed by the action of ferric chloride (*Puxeddu*, Gazz. 50, I, 149). By the action of light and air, anethole is slowly converted into *di-p*-methoxy-stilbene,  $\text{CH}_3\text{O}[4]\text{-C}_6\text{H}_4\text{CH}:\text{CHC}_6\text{H}_4[4']\text{OCH}_3$ , known as *photo-anethole* (*Höring*, Ber. 42, 1204). Anethole dibromide, m.p.  $67^\circ$  (*Hell*, J. pr. 52, 198). The oxidation of anethole with chromic acid gives anisic acid and acetic acid. With dilute nitric acid anisaldehyde is obtained (p. 346). With permanganate it gives methoxy-phenyl-glyoxylic acid (p. 427), and with mercuric acetate, anisyl-propylene-glycol (*Balbiano*, Ber. 35, 2997). With iodine and mercuric oxide, methoxy-hydratropaldehyde (see above) is formed. It combines with nitrous acid to give various products according to the conditions: **anethole pseudonitrosite**, **anethole nitrite**,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}(\text{NO})\cdot\text{CH}(\text{NO}_2)\text{CH}_3$ , m.p.  $121^\circ$ , *p*-methoxyphenyl-methyl-glyoxime,  $\text{CH}_3\text{OC}_6\text{H}_4\text{C}(\text{NOH})\text{C}(\text{NOH})\text{CH}_3$ , and the peroxide of the latter (see p. 408). Anethole nitrite when treated with acetyl chloride or sodium methylate loses hyponitrous acid and becomes  $\beta$ -nitroanethole,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}:\text{CH}(\text{NO}_2)\cdot\text{CH}_3$ , m.p.  $47^\circ$ , yellow needles. **Anethole-nitrosochloride**,  $(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CHCl}\cdot\text{CH}(\text{NO})\cdot\text{CH}_3$ , m.p.  $128^\circ$  (*Wallach*, Ann. 332, 318).

**o-Allyl-phenol**, **o-chavicol**,  $\text{HO}[2]\text{C}_6\text{H}_4\text{CH}_2\text{CH}:\text{CH}_2$ , b.p.  $220^\circ$ , b.p.  $99^\circ$  (12 mm.), is obtained from phenyl-allyl ether by thermal rearrangement (p. 193). **o,o**-Diallyl-phenol,  $\text{HO}[2]\text{C}_6\text{H}_3[1,3](\text{CH}_2\cdot\text{CH}:\text{CH}_2)_2$ , b.p.  $122^\circ$  (11 mm.). **o,o,p**-Triallyl-phenol, b.p.  $158-159^\circ$  (14 mm.). The methyl ether of *o*-allyl-phenol, *o*-estragol, b.p.  $86-87^\circ$  (12 mm.), is obtained from the phenol by the action of dimethyl sulphate and sodium hydroxide. Under the action of alkalis, *o*-

chavicol isomerises to *o*-propenyl-phenol, *o*-anol,  $\text{HO}[2]\text{C}_6\text{H}_4\text{CH}:\text{CHCH}_3$ , m.p. 37–38°; its methyl ether, *o*-anethole, b.p. 104–105° (13 mm.), is obtained from *o*-anol by methylation, or from *o*-estragol by rearrangement, or synthetically from methyl-salicylaldehyde. The oxidation of *o*-chavicol takes the same course as that of the *p*-compound, *o*-methoxyphenyl-acetaldehyde, or *o*-anisaldehyde and the corresponding acids being formed (*Claisen*, *Ann.* **418**, 69). *o*-Allyl-

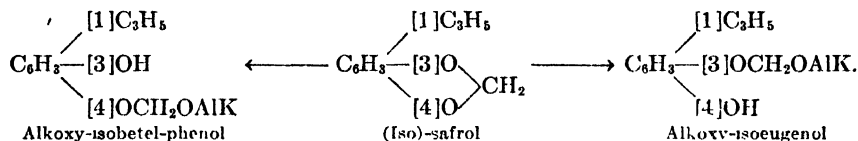
phenol condenses with hydrogen bromide to  $\text{C}_6\text{H}_4\begin{matrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{matrix} \text{C}:\text{CH}_3$ , 2-methyl-

coumarane. *m*-Propenyl-anisole, *m*-anethole, b.p. 227° (*Moureu*, *C.r.* **123**, 57; *Hell*, *Ber.* **36**, 1188). 4-Methyl-2-isopropenyl-phenol,  $\text{HO}[2]\text{CH}_3[4]\text{C}_6\text{H}_3\text{C}(\text{CH}_3):\text{CH}_2$ , m.p. 75° (containing ether of crystallisation), is obtained from *m*-cresol and acetone under the action of hydrogen chloride gas. When reduced catalytically, it gives thymol, and is therefore of some industrial importance (*Brit. Pats.* 273,684/5/6, 276,010, 279,855/6/7, 280,924, 280,956, and 306,051; *U. S. Pats.* 1,679,664, 1,696,769, and 1,706,784).

*o*-, *m*-, and *p*-Isopropenyl-anisole,  $(\text{CH}_3\text{O})\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}_3):\text{CH}_2$ , b.p. 199°, 215°, and 222° (m.p. 33°), are obtained from anisole-carboxylic esters and methyl magnesium iodide (*Behal*, *C.r.* **139**, 139; *Bull.* **3**, 301, 732). Like the propenyl-compounds, the isopropenyl compounds are readily reduced by sodium and alcohol. They are oxidised by permanganate to hydroxy-acetophenones. When their iodohydrins are treated with silver nitrate, ketones are formed, with migration of the aromatic residue (p. 281).

## 2. Olefine-dihydroxy-benzenes

The 3,4-dihydroxy-derivatives of this class, and more often their ethers, are constituents of essential oils, or have been isolated from the decomposition products of vegetable acids and alkaloids. Dihydroxy-benzenes are practically never found in natural products with their hydroxyl groups free, but occur as 3-methyl-, 3,4-dimethyl- or 3,4-methylene ethers. The free dihydroxy-benzenes are not easily obtained from these ethers without changes of the side-chains or resinification. When the methylene ethers are treated with alcoholic potash under pressure, allyl rearranges to propenyl (see above), while the methylene-dioxy group is split in two different ways, the elements of alcohol being taken up with the formation of two addition products:



When warmed with ethyl magnesium bromide, the methylene-dioxy compound gives alkoxy-isobetyl-phenol only (*Kuwata*, *Soc. Japan*, 1931, **34**, 212; *Kafuku*, *Pharm. Japan*, 1926). For other methods of opening the methylene-dioxy group, see *Paris*, *Rec.* **49**, 33.

Free vinyl-catechol,  $(\text{HO})_2[3,4]\text{C}_6\text{H}_2\text{CH}:\text{CH}_2$ , seems to be unstable and apt to polymerise. Its carbonate,  $\text{CO}(\text{O}_2)\text{C}_6\text{H}_2\text{CH}:\text{CH}_2$ , m.p. 66°, is obtained by dry distillation of 3,4-dihydroxy-benzylidene-malonic carbonate (*Pauly*, *Ber.* **41**,

4153). 3-Methyl-ether, vinyl-4,3-guaiacol,  $\text{CH}_3\text{O}[3] \begin{matrix} \diagup \\ \text{C}_6\text{H}_3\text{CH}:\text{CH}_2 \\ \diagdown \end{matrix}$ , m.p. 6–

8°, b.p. 114° (12 mm.), is obtained by the catalytic oxidation of di(*m*-methoxy-4-hydroxy-phenyl)-methyl-methane, or by splitting off carbon dioxide from ferulic acid (p. 476), and in small quantities, by the action of a *Grignard* reagent on vanillin (benzoate). The identity of these products with a vinyl-guaiacol occurring in beech-tar oil is still undecided (*Reichstein*, *Helv.* **15**, 1450). It is an oil with a strong smell of cloves. On oxidation it gives vanillin. Its 4-methyl-ether,

hesperitol, vinyl-3,4-guaiacol,  $\text{HO}[3] \begin{matrix} \diagup \\ \text{C}_6\text{H}_2\cdot\text{CH}:\text{CH}_2 \\ \diagdown \end{matrix}$ , m.p. 57°, is prepared by

dry distillation of calcium isoferulate (p. 476) (Tiemann, Ber. 14, 967). Vinyl-3,4-catechol-methylene ether,  $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3\text{CH}:\text{CH}_2$ , b.p. 108° (15 mm.), is

obtained from piperonal and magnesium methyl iodide (Klages, Ber. 36, 3595).

Allyl-3,4-catechol,  $(\text{HO})_2[3,4]\text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$ , m.p. 49°, b.p. 139° (4 mm.), has been detected in the oil of Java betel leaves. Its smell somewhat resembles that of creosote. Its alcoholic solution gives an intense green colour with ferric chloride (C. 1907, II, 1741). Allyl-2,3-catechol,  $(\text{HO})_2[2,3]\text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$ , m.p. 68°, and its 3,4-isomeride are the products of a thermal rearrangement of catechol-monoallyl-ether (Perkin, J. 1927, 1663). 1-*n*-Pentadecenyl-2,3-dihydroxy-benzene, uruschiol,  $(\text{HO})_2[2,3]\text{C}_6\text{H}_3\cdot\text{C}_{15}\text{H}_{29}$ , b.p. about 210° (0.5 mm.), is the chief constituent of Japanese shellac (Kurosawa, Ber. 48, 1603; Majima, Ber. 55, 172; see also Vol. II, p. 394).

Ethers of allyl-catechol are widely distributed in essential oils. The greatest industrial importance attaches to eugenol and safrol, which are the starting material in the preparation of the perfumes vanillin, and heliotropin (pp. 347, 349).

Eugenol, allyl-4,3-guaiacol,  $\text{HO}[4] \begin{array}{c} \diagup \\ \text{CH}_3\text{O}[3] \end{array} \text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$ , is an oil with a

strong odour of cloves, m.p. -7.5°, b.p. 254°,  $d_{15} 1.070$ . It gives a blue colour with ferric chloride. It occurs in clove oil from *Eugenia caryophyllata*, in pimento oil from *Pimenta acris*, and in the oil of cinnamon leaves. Tiemann (Ber. 9, 413) prepared it from coniferyl alcohol (p. 457) by the action of sodium amalgam. Claisen (Ann. 418, 69) synthesised it by introducing the allyl-group into guaiacol *o*-carboxylic acid, followed by the Claisen rearrangement, and removal of the carboxyl group. It is oxidised by permanganate to vanillin and vanillic acid. Heated with an excess of alcoholic potash it isomerises to *isoeugenol* (p. 453). For its hydrogenation to dihydro-eugenol, see *Ipatiew*, Ber. 46, 3589; *Br. Pat.* 352,663. For eugenol derivatives, see *Einhorn*, Ber. 27, 2455; *Hell*, Ber. 28, 2082).

Homoeugenol,  $\text{HO}[4] \begin{array}{c} \diagup \\ \text{CH}_3\text{O}[3] \end{array} \text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CHCH}_3$ , b.p. 144-146° (12 mm.), is

obtained by hydrogenation of vanillylidene-acetone under pressure, the 4-hydroxy 3-methoxyphenyl-butanol formed being dehydrated with 60% sulphuric acid

(Arch. Pharm. 265, 104). *o*-Eugenol,  $\text{HO}[2] \begin{array}{c} \diagup \\ \text{CH}_3\text{O}[3] \end{array} \text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$ , b.p. 122° (12 mm.), an oil with a strong smell of cloves, has been obtained by thermal rearrangement of guaiacol-allyl ether (Claisen, Ann. 401, 50).

Chavibetol, betel-phenol, allyl-3,4-guaiacol,  $\text{CH}_3\text{O}[3] \begin{array}{c} \diagup \\ \text{CH}_3\text{O}[4] \end{array} \text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$ ,

m.p. 8.5°, b.p. 254°, occurs in the essential oil of the leaves of *Piper betle* (Bertram, J. pr. 39, 349; Eykman, Ber. 23, 862). Under the influence of caustic potash it rearranges to isobetel-phenol (see below).

Eugenol-methyl ether, allyl-3,4-veratrol,  $\text{HO}[3] \begin{array}{c} \diagup \\ \text{CH}_3\text{O}[4] \end{array} \text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$ , m.p.

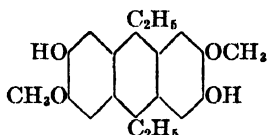
-3.7°, b.p. 244°, occurs in paracote oil (Wallach, Ann. 271, 304), in the essential oil of *Asarum europaeum* (Petersen, Ber. 21, 1060), in bay oil, and to a large extent in the wood oil of *Dacrydium Franklinii*, etc. It has been synthesised by Moureu (C.r. 121, 721) from pyrocatechol dimethyl ether, allyl iodide, and zinc dust. It has also been obtained from sodio-eugenol or potassio-chavibetol by the action of methyl iodide (Bertram, J. pr. 39, 353). It is oxidised by chromic acid to dimethyl-protocatechuic acid (veratric acid, p. 366) and by heating with alcoholic potash it is converted into isoeugenol.

Safrol, shikimol, allyl-3,4-catechol-methylene ether,  $\text{CH}_2 \begin{array}{c} \diagup \text{O}[3] \diagdown \\ \diagdown \text{O}[4] \diagup \end{array} \text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$ , m.p. 11°, b.p. 233°, is found in the oils from *Sassafras officinale* and *Illicium religiosum* or *Shikimino-Ki*, and in oil of camphor. It is prepared from

the last industrially. Dibromide, m.p. 87°. When ozonised it gives homopiperonal,  $\text{CH}_2 \begin{matrix} \text{O[3]} \\ \text{O[4]} \end{matrix} \text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ , b.p. 131–133° (8 mm.) (*Nagai*, J. Tokyo, 1923). When oxidised with permanganate it gives *m,p*-methylene-dioxybenzyl glycol (p. 399), homopiperonylic acid (p. 368), and piperonyl-carboxylic acid (p. 427), which can be further oxidised to piperonal and piperonylic acid (p. 366) (*Wagner*, Ber. 24, 2488; *Hell*, Ber. 28, 2088). On heating with caustic alkalis (p. 419) safrol isomerises to isosafrol (see below). For nitrosites see *Angeli*, Gazz. 25, II, 188. For 6-nitro- and 6-amino-safrol, see *Foulds*, J. 105, 1963.

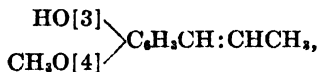
Propenyl-3,4-pyrocatechol,  $(\text{HO})_2[3,4]\text{C}_6\text{H}_3\text{CH}:\text{CH}\cdot\text{CH}_3$ , m.p. 105.5°, isomeric with allyl-3,4-catechol, is obtained from its diacetate, m.p. 96°, by the action of ammonia on its ether solution (the diacetate is formed by the action of sodium acetate and acetic anhydride on alkoxy-isoeugenol) (*Hiraidzum*, Soc. Japan, 34, 208). Small quantities are formed in the reaction between protocatechuic aldehyde and an excess of ethyl magnesium bromide (*Behal*, Bull. 3, 301). Isoeugenol, its methyl ether, and isosafrol are derived from this compound. They are propenyl-catechol ethers, isomeric with the allyl-catechol ethers just described.

Isoeugenol, propenyl-4,3-guaiacol,  $\text{HO[4]CH}_3\text{O[3]C}_6\text{H}_3\text{CH}:\text{CH}\cdot\text{CH}_3$ , forms a solid *trans*-modification, m.p. 34°, and a liquid *cis*-modification, b.p. 115° (5 mm.) (*Boedecker*, Ber. 64, 61). It occurs in ylang-ylang and nutmeg oil, and has been prepared by distilling homoferulic acid (p. 477) with lime, by heating eugenol in amyl alcohol with caustic potash of sodium ethylate (*Tiemann*, Ber. 27, 2580), and synthetically by the action of ethyl magnesium bromide on vanillin (*Behal*, Bull. 3, 301). Isoeugenol is converted by alcoholic or ethereal hydrogen chloride into a compound known as *di-isoeugenol*, m.p. 179–180°, which has been shown by *Havorth* and *Marin* (J. 1931, 1363) to be 2,6-dihydroxy-3,7-dimethoxy-9,10-dihydro-anthracene:



When isoeugenol is oxidised, its hydroxyl-group being temporarily protected by acetylation, vanillin is formed. This reaction is carried out on the large scale. *cis*-Phenyl-urethane, m.p. 118°; benzoate, m.p. 68°; *trans*-phenyl-urethane, m.p. 152°; acetate, m.p. 79°.

Isobetel-phenol, isochavibetol, propenyl-3,4-guaiacol,



m.p. 96°, is obtained by rearrangement of betel-phenol with caustic potash, and from alkoxy-isoeugenol (p. 451) by methylating the hydroxy-group and then removing the  $\text{CH}_2\text{OAlk}$  group by boiling with slightly acidified alcohol. The methylation of isoeugenol and isobetel-phenol gives

Isoeugenol methyl ether, propenyl-3,4-veratrol, b.p. 263°, which is known in two stereoisomeric forms, one solid, m.p. 17.4°, and the other a liquid (*Boedecker*, Ber. 64, 61). It has been detected in the oil of *Asarum arifolium*. It is prepared artificially from eugenol-methyl ether by warming with alcoholic potash (*Ciamician*, Ber. 23, 1165), from isoeugenol and isobetel-phenol by methylation, and from O-methyl-vanillin by the action of ethyl magnesium bromide (*Behal*, Bull. 3, 301). It is oxidised by permanganate to veratroyl-carboxylic acid (p. 427) and veratric acid (*Tiemann*, Ber. 24, 2877). On careful oxidation, a glycol, m.p. 88°, is formed (p. 399) (*Balbiano*, Ber. 36, 3582). *o*-Isoeugenol,

$\text{HO}[2] \rangle \text{C}_6\text{H}_3\text{CH}:\text{CHCH}_3$ , m.p.  $78^\circ$ , is obtained from *o*-eugenol by isomerisation with caustic potash (Claisen, Ann. 418, 69) or from *o*-vanillin with ethyl magnesium bromide (Doutteau, Bull. 11, 652).

Isosafrol,  $\text{CH}_2 \begin{matrix} \text{O}[3] \\ \text{O}[4] \end{matrix} \rangle \text{C}_6\text{H}_3\text{CH}:\text{CH}\cdot\text{CH}_3$ , exists in two stereoisomeric forms; the *cis*-form is unstable, b.p.  $242\text{--}243^\circ$ , and the *trans* is stable, b.p.  $247\text{--}248^\circ$  (Schimmel's Ber., 1922, 162). It is obtained from safrol by warming with alcoholic potash or dry sodium ethylate, and synthetically by the action of ethyl magnesium bromide on piperonal (Mameli, Lincoi 13, II, 315). Dibromide, m.p.  $52\text{--}53^\circ$ . Like isoeugenol, it dimerises under the influence of hydrogen chloride or formic acid. On heating, or with stannic chloride, higher polymers with molecular weights up to 1600 are obtained. It is oxidised by permanganate or mercuric acetate to a glycol (p. 399), m.p.  $101^\circ$  (Balbiano, Ber. 36, 3580), and to piperonyl-carboxylic acid (p. 427). With chromic acid, isosafrol gives piperonal, artificial heliotropin, from which it is regenerated by condensation with propionic acid, carbon dioxide being removed from the methylene-homocaffeic acid (p. 477) first formed (Moureau, C.r. 122, 792; Wallach, Ber. 357, 77). For the opening of the methylene-dioxy group, see above. Reduction with sodium and alcohol converts isosafrol into dihydro-safrol and *m*-propyl-phenol (Ipatiev, Ber. 46, 3589). Pseudonitrosite, m.p.  $128^\circ$  (Wallach, Ber. 332, 331).

For the so-called safro-eugenol,  $\text{HO}[3] \rangle \text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$ , safro-isoeugenol, and related substances, see Kafuku, Pharm. Japan, 1925.

### 3. Olefine-trihydroxy-benzenes

Asarone, propenyl-2,4,5-trimethoxy-benzene,  $(\text{CH}_3\text{O})_3[2,4,5]\text{C}_6\text{H}_3\text{CH}:\text{CH}\cdot\text{CH}_3$ , m.p.  $61^\circ$ , b.p.  $296^\circ$ , can be isolated from the essential oil of *Asarum europaeum*, and from calamus oil (Thoms, Ber. 35, 3190), in which it accompanies terpenes and eugenol. It has been synthesised from asaraldehyde (p. 350), propionic anhydride, and sodium propionate (Gattermann, Ber. 32, 289). It is oxidised by permanganate to asaraldehyde, 2,4,5-trimethoxy-benzaldehyde (p. 350), and asaronic acid, 2,4,5-trimethoxy-benzoic acid. When the latter is distilled with lime it decomposes into carbon dioxide and hydroxyhydroquinone-trimethyl ether (p. 232) (Ciamician, Ber. 23, 2294).

Elemicin, allyl-3,4,5-trimethoxy-benzene,  $(\text{CH}_3\text{O})_3[3,4,5]\text{C}_6\text{H}_3\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , b.p.  $144\text{--}147^\circ$  (10 mm.), is the chief constituent of Manila elemi oil (Semmler, Ber. 41, 1768). It has been synthesized by Mauthner (Ann. 414, 250) by subjecting pyrogallol-allyl-2,6-dimethyl ether to the Claisen transformation, followed by methylation of the free OH group formed. On ozonisation it gives trimethyl-ether-homogallaldehyde, and trimethyl-ether-homogallallic acid, and when treated with permanganate in acetone solution it gives trimethyl-ether-gallallic acid. On heating with alcoholic potash, it changes to the corresponding propenyl compound, isoelemicin, b.p.  $153\text{--}156^\circ$  (10 mm.), which is a position isomer of asarone, and which is oxidised to trimethyl-ether-gallaldehyde and trimethyl-ether-gallallic acid by ozone (Semmler, Ber. 41, 1918, 2556).

Myristicin, allyl-3,4,5-trihydroxybenzene-methylene methyl ether,  $\begin{matrix} (\text{CH}_2\text{O})_2 \\ (\text{CH}_2\text{O}) \end{matrix} \rangle \text{C}_6\text{H}_3\text{CH}_2\text{CH}:\text{CH}_2$ , an oil, b.p.  $149^\circ$  (15 mm.). It can be extracted from the high-boiling fractions of nutmeg and mace oils, and together with apiol, from French parsley seed (Thoms, Ber. 36, 3451). It is converted into the propenyl compound, isomyristicin, m.p.  $45^\circ$ , which occurs in mace and dill oils, by treatment with alcoholic potash, and on oxidation with permanganate it gives myristicin aldehyde, m.p.  $131^\circ$ , and myristicin acid, m.p.  $208\text{--}209^\circ$  (Thoms, Ber. 36, 3446). For nitrosites, see Rimini, Gazz. 35, I, 406.

3,4,5-Trimethoxy- $\omega$ -nitrostyrene,  $(\text{CH}_3\text{O})_3[3,4,5]\text{C}_6\text{H}_3\text{CH}:\text{CHNO}_2$ , m.p.  $119\text{--}120^\circ$ , is obtained from trimethyl-ether-gallaldehyde (Mauthner, J. pr. 92, 194).

## 4. Olefine-tetrahydroxy-benzenes

**Apiole**, allyl-apionol-dimethyl-methylene-ether,  $(\text{CH}_3\text{O})_2[2,5](\text{CH}_2\text{O})[3,4]-\text{C}_6\text{H}-\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , m.p.  $30^\circ$ , b.p.  $294^\circ$ , occurs in parsley seed from *Petroselinum sativum*, etc. When oxidised with permanganate it forms ethers of the corresponding tetrahydroxy-benzaldehyde and acid; see also apionol, p. 232. When boiled with alcoholic potash, it changes to the isomeric propenyl derivative, *isoapiol*, m.p.  $56^\circ$ , b.p.  $304^\circ$  (Bartolotti, Gazz. 22, I, 558; Thoms, Ber. 36, 1714). An isomer of parsley apiole, distinguished from it by the position of one of the methoxy-groups, is the so-called dill-apiole,  $(\text{CH}_3\text{O})_2[5,6](\text{CH}_2\text{O})[3,4]-\text{C}_6\text{H}-\text{CH}_2\text{CH}:\text{CH}_2$ , b.p.  $285^\circ$ , found in oil of dill from *Anethum graveolens* (Ciamician, Ber. 29, 1800), in sea-fennel oil (Delepine, Bull. 5, 926), in bamba oil (Spoelstra, Rec. 48, 372), and together with parsley apiole, in matico oil. With alcoholic potash it isomerises to dill-isoapiole, m.p.  $44^\circ$  (Thoms, Arch. Pharm. 242, 344). 1-Allyl-2,3,4,5-tetramethoxy-benzene,  $(\text{CH}_3\text{O})_4[2,3,4,5]-\text{C}_6\text{HCH}_2\text{CH}:\text{CH}_2$ , m.p.  $25^\circ$ , has been isolated from French parsley seed oil. With permanganate it gives 2,3,4,5-tetramethoxy-benzoic acid, m.p.  $87^\circ$  (Thoms, Ber. 41, 2761).

## IIb. Acetylene-Phenols

**Acetylene-anisole**,  $\text{CH}:\text{CC}_6\text{H}_4\text{OCH}_3$ , b.p.  $85-88^\circ$  (11 mm.), is obtained from  $\alpha,\beta$ -dichloro-*p*-methoxy-styrene, by the action of sodium (Kunckell, Ber. 36, 915), and from *p*-methoxy-bromostyrene, by the action of alcoholic potash (Manchor, Ann. 387, 257). **Acetylene-phenetol**,  $\text{CH}:\text{C}\cdot\text{C}_6\text{H}_4\text{O}\cdot\text{C}_2\text{H}_5$  (Fittig, Ann. 269, 13).

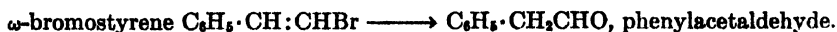
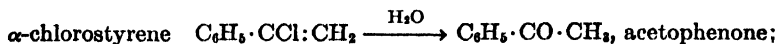
**3,4-Methylene-dioxyphenyl-acetylene**,  $\text{CH}_2 \begin{array}{c} \diagup \text{O}[3] \\ \diagdown \text{O}[4] \end{array} \text{C}_6\text{H}_3\text{C}:\text{CH}$ , *piperonyl-acetylene*, b.p.  $103^\circ$  (11 mm.), is obtained from piperonal and malonic acid, via methylene-dioxy-cinnamic acid (p. 477), its dibromide, and methylene-dioxy- $\omega$ -bromostyrene (Lohaus, J. pr. 119, 235). **3,4-Methylene-dioxyphenyl-propine**, *piperonyl-propine*,  $\text{CH}_2\text{O}_2[3,4]-\text{C}_6\text{H}_3\text{C}:\text{CCH}_3$ , m.p.  $42-43^\circ$ , is obtained from isosafrol dibromide via bromo-isosafrol, which is treated with alcoholic potash (Foulda, J. 105, 1963).

## III. The Phenyl Olefine Alcohols and Their Oxidation Products

The chemistry of the phenyl olefine alcohols, aldehydes and ketones is less developed than that of the phenyl paraffin alcohols and their oxidation products. The most important representatives of this class will be described below, together with their derivatives of phenolic type. The detailed scheme of classification of poly-alcohols and their oxidation products, which has been used in the case of the mononuclear benzene derivatives with saturated oxygen-containing side-chains, will not be followed here, because no representatives of many of the theoretically possible groups of compounds with unsaturated oxygen-containing side-chains have yet been prepared. Compounds of this type will be discussed together with the nearest related simple phenyl olefine alcohols and their oxidation products.

## 1a. Phenyl Olefine Alcohols

Neither of the two theoretically possible phenyl-vinyl alcohols is known, and possibly they do not exist. When the halogen atom of an  $\alpha$ -halogeno-styrene is replaced by hydroxyl, acetophenone is formed, and from an  $\omega$ -halogeno-styrene, phenyl-acetaldehyde is obtained:





The corresponding ethers, the alkoxy-styrenes, have however been prepared, together with the  $\omega$ -acetate (Ley, Ber. 51, 1818; Sigmund, Mo. 51, 234).

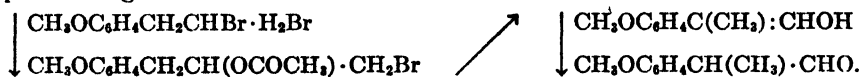
$\beta$ -Phenyl-vinyl-methyl ether, b.p. 210–213°, and  $\beta$ -phenyl-vinyl-ethyl ether,  $C_6H_5 \cdot CH:CH \cdot OC_2H_5$ , b.p. 115° (24 mm.), is obtained from  $\omega$ -halogeno-styrenes (p. 444) or from phenyl-acetylene by heating with sodium ethoxide (Nef, Ann. 308, 270; Moureu, C.r. 138, 286). A stereoisomeric form is obtained from the diethyl-acetal of phenyl-acetaldehyde by removing alcohol from it (Dufraisse, Bull. 39, 905).  $\alpha$ -Phenyl-vinyl-methyl ether,  $C_6H_5C(OCH_3):CH_2$ , b.p. 197°, is obtained from  $\beta$ -methoxycinnamic acid.  $\alpha$ -Phenyl-vinyl-ethyl ether,  $C_6H_5C(OC_2H_5):CH_2$ , m.p. 209°, can be obtained by heating acetophenone acetal (p. 283), when alcohol is lost, or by heating  $\beta$ -ethoxy-cinnamic acid. When heated under pressure, it isomerises to phenyl-ethyl ketone (p. 282) (Claisen, Ber. 29, 2931). When these ethers are hydrolysed, phenyl-acetaldehyde and acetophenone are formed (Moureu, C.r. 138, 286).  $\beta$ -Phenyl-vinyl-phenyl ether,  $C_6H_5 \cdot CH:CH \cdot OC_6H_5$ , b.p. 158° (7 mm.), is obtained by distilling  $\alpha$ -phenoxy-cinnamic acid. When it is heated at about 200° with alcoholic potash,  $\beta$ -phenyl-vinyl-ethyl ether is formed among other products, the phenol residue being displaced (Stoermer, Ber. 38, 1962).  $\beta$ -Phenyl-vinyl-acetate, "styryl acetate,"  $C_6H_5CH:CHO \cdot COCH_3$ , *cis*-form m.p. 33°, *trans*-form b.p. 128° (15 mm.), is hydrolysed to phenyl-acetaldehyde (Semmler, Ber. 42, 589; Boeseken, Rec. 52, 14).

Cinnamyl alcohol, "styrone,"  $\gamma$ -phenyl-allyl alcohol, m.p. 33°, b.p. 258°, occurs as the cinnamic ester in liquid storax, the sap of a tree, *Liquidambar orientalis*, found in the south-west of Asia Minor, and in other plants. It is made artificially by reducing cinnamic aldehyde or its diacetate also by an exchange of oxidation levels (U. S. Pat. 1,688,033). By the reduction of the diethyl-acetal of phenyl-propargaldehyde (p. 461), a substance is obtained which appears to be a stereoisomeric *cis*-cinnamyl alcohol. Its smell is more pleasant than that of the ordinary *trans* form (Bourguet, Bull. 45, 1067). On oxidation, it gives cinnamic aldehyde, cinnamic acid, and benzoic acid; see also stycerol, p. 399. Cinnamylamine, *styrylamine*,  $C_6H_5 \cdot CH:CH \cdot CH_2OH$ , b.p. 236° (Posner, Ber. 26, 1858; Ende, Arch. Pharm. 244, 269). For cinnamyl-alkyl ethers, see Beaufour, Bull. 11, 648). Cinnamyl chloride,  $C_6H_5CH:CHCH_2Cl$ , m.p. 7–8°, b.p. 115° (13 mm.), is obtained from cinnamyl alcohol and hydrochloric acid (Dupont, C. 1910, II, 734), or thionyl chloride (Gilmore, Rec. 50, 1052) and cinnamyl bromide, m.p. 31–32°, is obtained in a similar manner. These halides show some anomalous reactions. The chloride reacts with magnesium giving a compound,  $C_6H_5CH(MgCl)CH:CH_2$ , which forms, with carbon dioxide, phenyl-vinyl-acetic acid,  $C_6H_5CH(COOH)CH:CH_2$ , and the bromide, on hydrolysis with alcoholic potash, gives partly cinnamyl-ethyl ether, and partly an isomeric ether, *viz.*, that of phenyl-vinyl carbinol (Meisenheimer, Ann. 479, 214; Gilman, Am. 53, 3541). This carbinol,  $\alpha$ -phenyl-allyl alcohol,  $C_6H_5CH(OH)CH:CH_2$ , b.p. 114° (25 mm.), has also been prepared from phenyl magnesium bromide and acrolein (Klages, Ber. 39, 2554), and from hydroxymethylene-acetophenone by catalytic reduction, water being eliminated (Rupe, Helv. 4, 841). Its acetate is obtained by the action of potassium nitrate or silver nitrate on cinnamyl chloride, together with cinnamyl acetate (Meisenheimer, Ann. 508, 58). For homologous vinyl-aryl carbinols, see Delaby, C.r. 194, 1248.

Styryl-methyl carbinol,  $\gamma$ -phenyl- $\alpha$ -methyl-allyl alcohol,  $C_6H_5 \cdot CH:CHCH(CH_3)OH$ , b.p. 144° (21 mm.), is obtained by the action of methyl magnesium iodide on cinnamic aldehyde (Klages, Ber. 35, 2649; Sand, *ibid.*, 3186).

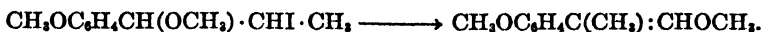
### 1b. Hydroxyphenyl Olefine Alcohols

$\beta$ -Anisyl- $\alpha$ -methyl-vinyl alcohol,  $CH_3OC_6H_4C(CH_3):CHOH$ , m.p. 79°, b.p. 175° (14 mm.), is obtained from estragal dibromide by successive treatment with potassium acetate and alcoholic potash, a molecular rearrangement taking place during the reaction:

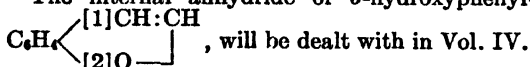


This alcohol, when distilled at ordinary pressure, or subjected to the influence of an acid, changes to *p*-methoxy-hydratropic aldehyde. With sodium methylate

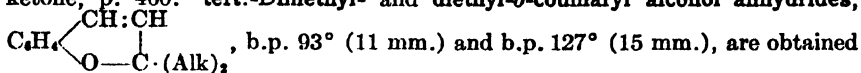
or dimethyl sulphate, it gives a methyl ether, b.p. 262°, which is also obtained from anethole-methyl iodohydrin by treatment with mercuric oxide, when a migration of the aromatic residue occurs (*Tiffeneau*, C.r. 145, 593, 628):



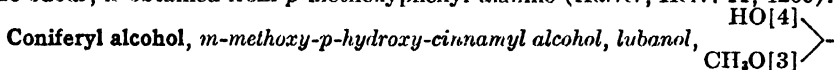
The internal anhydride of *o*-hydroxyphenyl-vinyl alcohol, or *coumarone*,



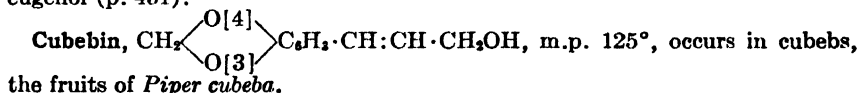
**Glyco-*o*-coumaryl alcohol**,  $\text{C}_6\text{H}_{11}\text{O}_5 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2\text{OH}$ , m.p. 115°, is obtained from glyco-*o*-coumaraldehyde (p. 459). **sec.-Methyl-*o*-coumaryl alcohol**,  $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CH}(\text{OH})\text{CH}_3$ , m.p. 47°, see methyl-*o*-coumaryl ketone, p. 460. **tert.-Dimethyl- and diethyl-*o*-coumaryl alcohol anhydrides**,



from coumarin (p. 474) by the action of methyl magnesium iodide, and ethyl magnesium iodide (*Houben*, Ber. 37, 494). ***p*-Methoxy-cinnamyl alcohol**,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_4\text{CH} : \text{CHCH}_2\text{OH}$ , m.p. 79–80°, possessing a very pleasant flower-like odour, is obtained from *p*-methoxyphenyl-alanine (*Karrer*, Helv. 11, 1209).



is a viscous non-volatile oil. Its glycoside is coniferin (Vol. II, p. 357), which is decomposed by emulsin into glucose and coniferyl alcohol. It is also obtained from its aldehyde (p. 459) by reduction with yeast (*Pauly*, Ber. 62, 297). On oxidation it gives vanillin, and on reduction, isoeugenol (p. 451).



### 1c. Phenyl-acetylene Alcohols

These are obtained by condensing sodio-phenyl-acetylene suspended in ether with trihydroxy-methylene- or homologous aldehydes, or by the action of caustic potash on a mixture of ketones and phenyl-acetylene, or by the action of alkyl magnesium halides on phenyl-propargaldehyde or phenyl-acetylene ketones. **Phenyl-acetylene alcohol, phenyl-propargyl alcohol**,  $\text{C}_6\text{H}_5\text{C} : \text{C} \cdot \text{CH}_2\text{OH}$ , b.p. 140° (12 mm.), is obtained from phenyl-acetylene and formaldehyde by the action of ethyl magnesium bromide (*Guest*, Am. 47, 860), and from the dibromide of cinnamyl acetate by the action of alcoholic potash (*Bert*, C.r. 191, 493). **Phenyl-propargyl bromide**,  $\text{C}_6\text{H}_5\text{C} : \text{C} \cdot \text{CH}_2\text{Br}$ , b.p. 135° (15 mm.) is obtained by the action of phosphorus tribromide on the alcohol (*Braun*, Ann. 458, 102). **Phenyl-acetylene-methyl carbinol**,  $\text{C}_6\text{H}_5\text{C} : \text{C} \cdot \text{CH}(\text{OH})\text{CH}_3$ , b.p. 149° (29 mm.). **Phenyl-acetylene-dimethyl carbinol**,  $\text{C}_6\text{H}_5\text{C} : \text{C} \cdot \text{CC}(\text{OH})(\text{CH}_3)_2$ , m.p. 53°. **Heptyl-phenyl carbinol**,  $\text{CH}_3(\text{CH}_2)_5\text{C} : \text{C} \cdot \text{CH}(\text{OH})\text{C}_6\text{H}_5$ , b.p. 181° (16 mm.), is obtained from sodio-heptyl and benzaldehyde (*Klages*, Ber. 39, 2554; *Moureu*, C.r. 132, 1223; 134, 355; *Brachin*, Bull. 35, 1163). **Phenyl-methyl-ethynyl carbinol**,  $\text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{C} : \text{CH} \end{array} \text{CH}_2$ , m.p. 49°, b.p. 102–103° (12 mm.), is obtained from acetophenone and acetylene with sodium or sodamide. When boiled with formic acid it is converted into  $\beta$ -methyl-cinnamaldehyde,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3) : \text{CH} \cdot \text{CHO}$ , (*Rupe*, Helv. 11, 656).

### 2a. Phenyl Olefine Aldehydes

**CINNAMIC ALDEHYDE**,  $\beta$ -phenyl-acrolein,  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CHO}$ , m.p. –7.5°, b.p. 252°, is the principal ingredient of cinnamon bark oil from *Cinnamomum ceylanicum*, and of cassia oil from the leaves and sprigs of *Cinnamomum*.

*cassia*, from which it is extracted with sodium bisulphite. First a sparingly soluble double compound of the formula,  $C_6H_5 \cdot CH:CH \cdot CH(OH)SO_2Na$ , is formed, and then, with another molecule of the bisulphite, sodium sulpho-cinnamaldehyde sulphite,  $C_6H_5 \cdot CH(SO_2Na) \cdot CH_2 \cdot CH(OH)SO_2Na + 2H_2O$ , is formed, which is soluble in water (*Heusler*, Ber. 24, 1805; *Tiemann*, Ber. 31, 3301). Cinnamyl aldehyde is obtained by the oxidation of cinnamyl alcohol, by the dry distillation of a mixture of calcium cinnamate and formate, and by the action of hydrogen chloride, aqueous sodium hydroxide, or sodium ethylate on a mixture of benzaldehyde and acetaldehyde (*Peine*, Ber. 17, 2117; *Claisen*, Ber. 20, 657). It has also been obtained from cinnamyl chloride by catalytic reduction in the presence of a partially poisoned catalyst (*Rosenmund*, Ber. 56, 1481). By reducing phenyl-propargaldehyde diacetal, *Bourguet* (Bull. 45, 1067) has prepared what is believed to be the diacetal of an isomeric *cis*-cinnamic aldehyde. Dimethyl-acetal, b.p. 126° (11 mm.). Diacetate, m.p. 85° (*Thiele*, Ann. 306, 253). The reduction of cinnamic aldehyde has been studied by *Skita* (Ber. 48, 1486, 1686); *Meerwein* (Ann. 444, 221); *Verley* (Bull. 37, 537); *Tuley* (Am. 47, 3061); and *Shima* (Mem. Kyoto, 12, 69).

Cinnamic aldehyde is an oil with an aromatic odour, and a high refractive index. It is volatile with steam. It oxidises in air to cinnamic acid. It adds on chlorine and bromine, and the dihalides formed readily go over into  $\alpha$ -monochloro- and  $\alpha$ -monobromo-cinnamaldehydes,  $C_6H_5 \cdot CH:CH \cdot CX \cdot CHO$ , m.p. 35° and 72°, respectively (*Naar*, Ber. 24, 246). Cinnamal dichloride,  $C_6H_5CH:CH \cdot CHCl_2$ , m.p. 54°, b.p. 143° (30 mm.), behaves as an acid chloride, but combines with chlorine, and forms phenyl-tetrachloro-propane,  $C_6H_5CHCl \cdot CHCl \cdot CHCl_2$  (*Charon*, C.r. 136, 94, 1072).  $\alpha$ - and  $\beta$ -Trithio-cinnamic aldehydes, m.p. 167 and 213°, respectively (*Baumann*, Ber. 24, 1452).

Hydrocinnamide,  $N_2(CH \cdot CH:CH \cdot C_6H_5)_2 + \frac{1}{2} H_2O$ , m.p. 106° and 131° (anhydrous). Cinnam-phenylhydrazone, m.p. 168°; *syn*-oxime, m.p. 138.5°; the *anti*-oxime, m.p. 76°, changes into the *syn*-oxime on treatment with hydrogen chloride. The *syn*-oxime, however, has not yet been obtained free from the *anti*-compound (*Bamberger*, Ber. 27, 2795; *Brady*, J. 121, 2098). When heated with phosphorus pentoxide, the *syn*-oxime gives isoquinoline (*Goldschmidt*, Ber. 27, 2795). With hydrazine hydrate, cinnamic aldehyde forms 3-phenyl-pyrazoline (*Freudenberg*, Ann. 440, 38). With nitric acid, snow-white crystals of a fairly stable addition-product, m.p. 60–61°, are formed (*Reddelien*, J. pr. 91, 213). The chief product of the action of oxides of nitrogen on cinnamic aldehyde is

phenyl-nitro-oxazole,  $\begin{array}{c} \text{O} \cdot \text{N} : \text{C}(\text{C}_6\text{H}_5 \cdot) \text{C}(\text{NO}_2) : \text{CH} \end{array}$  (*Wieland*, Ann. 328, 196).

*o*-, *m*-, and *p*-Nitro-cinnamic aldehydes, m.p. 127°, 116°, and 141°, respectively, are obtained from the nitrophenyl-hydracrylic aldehydes (p. 403) (*Diehl*, Ber. 18, 2335).

$\alpha$ -Methyl-cinnamic aldehyde,  $C_6H_5 \cdot CH:C(CH_3)CHO$  (*Miller*, Ber. 19, 526, 1248).  $\beta$ -Methyl-cinnamic aldehyde see above, p. 457. Among the homologous alkyl-cinnamic aldehydes (*Heller*, Ber. 55, 483; *Shorigin*, Russ. 62, 2033; Br. Pat. 234,458),  $\alpha$ ,*n*-amyl-cinnamic aldehyde,  $C_6H_5CH:C(C_5H_{11}) \cdot CHO$ , b.p. 140° (5 mm.), is of importance industrially, because it has a strong odour of jasmine, especially when diluted. It is known as *jasmilan*, *flosal*, etc. It is prepared from benzaldehyde, oenanthol, and dilute sodium hydroxide (*Rutowski*, J. pr. 119, 272).  $\alpha$ -Phenyl- and  $\alpha$ -benzyl-cinnamic aldehydes, m.p. 94–95°, and 53–54°, respectively, are obtained from benzaldehyde by the action of phenyl-acetaldehyde and hydrocinnamic aldehyde, respectively (*Schorigin*, Ber. 66, 389).

Atropic aldehyde,  $\alpha$ -phenyl-acrolein,  $C_6H_5C(:CH_2) \cdot CHO$ , b.p. 96° (12 mm.), is obtained from atropyl chloride through the anilide, the phenyl-imide chloride, and reduction with chromous chloride (*Braun*, Ber. 67, 269).

$\gamma$ -Benzyl-crotonic aldehyde,  $C_6H_5CH_2CH_2CH:CHCHO$ , b.p. 139° (13 mm.), has been prepared from hydrocinnamic aldehyde by the action of acetaldehyde (*Fischer*, Ber. 31, 1993).

## 2b. Hydroxyphenyl Olefine Aldehydes

Compounds with a free hydroxyl-group are obtained by condensing hydroxy-benzaldehydes with acetaldehydes by means of dilute alkalis. During the reac-

tion, the hydroxyl group must be protected by some group that can easily be removed later. Alkoxy-compounds are prepared in a similar manner from alkoxy-benzaldehydes (Pauly, Ber. 56, 603). *o*-Coumaric aldehyde, *o*-hydroxycinnamic aldehyde,  $\text{HO}[2]\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CHO}$ , m.p.  $133^\circ$ , is liberated by emulsin from glyco-*o*-coumaric aldehyde,  $\text{C}_6\text{H}_4\text{O}_5\cdot\text{O}\cdot\text{C}_6\text{H}_4\text{CH}:\text{CH}\cdot\text{CHO}$ , m.p.  $199^\circ$ , the condensation product of helicin (Vol. II, p. 355) and acetaldehyde (Miller, Ber. 20, 1931). Its methyl ether occurs in oil of cassia (Bertram, J. pr. 51, 316). *p*-Methoxy-cinnamic aldehyde, *p*-methyl-coumaric aldehyde, m.p.  $134^\circ$ , b.p.  $170^\circ$  (14 mm.), has been found in tarragon oil (Daufresne, Bull. Pharm. 15). By further condensation with acetaldehyde it is converted into *p*-methoxycinnamylidene-acetaldehyde. Both these aldehydes form liquid crystals. *m*- and *p*-Hydroxycinnamic aldehyde-*O*-acetic acids,  $\text{COOH}\cdot\text{CH}_2\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CHO}$ . (Elkan, Ber. 19, 3049). *p*-Hydroxy-*m*-methoxy-cinnamic aldehyde, coniferaldehyde, ferulic aldehyde,

$\text{HO}[4]\text{C}_6\text{H}_3\text{CH}:\text{CH}\cdot\text{CHO}$ , m.p.  $82.5^\circ$ , is a decomposition product of lignin under the action of alkali or acid, and has been synthesised from vanillin (Pauly, Ber. 56, 603; 62, 297; Hoffmeister, Ber. 60, 2062; Klason, Ber. 61, 171). For geometrical isomers of coniferaldehyde see Ber. 63, 912. *o*-Coniferaldehyde, m.p.  $131^\circ$ , is obtained from *o*-vanillin.

Piperonyl-acrolein,  $(\text{CH}_3\text{O})_2[3,4]\text{C}_6\text{H}_3\text{CH}:\text{CH}\cdot\text{CHO}$ , m.p.  $84-85^\circ$ , is obtained from piperonal, acetaldehyde, and sodium hydroxide (Ott, Ber. 55, 2662; Lohaus, J. pr. 119, 235). See also piperinic acid.

### 3. Phenyl Polyolefine Aldehydes

Cinnamylidene-acetaldehyde,  $\text{C}_6\text{H}_5\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CHO}$ , b.p.  $160-162^\circ$  (20 mm.), and 7-phenyl-heptatrienal,  $\text{C}_6\text{H}_5\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CHO}$ , b.p.  $190-195^\circ$  (16 mm.), are both contained in the higher boiling fractions in the industrial process of preparing cinnamic aldehyde. They are obtained from cinnamic aldehyde and acetaldehyde (Vorländer, Ber. 58, 1284; 62, 541). *o*-Nitrocinnamylidene-acetaldehyde,  $\text{NO}_2\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CHO}$ , m.p.  $153^\circ$  (Einhorn, Ber. 17, 2026).

#### 4a. Phenyl Olefine Ketones

Phenyl olefine ketones are readily obtained by condensing aromatic aldehydes with aliphatic ketone containing  $\text{CH}_3$ , or  $\text{CH}_2\text{R}$  groups, in addition to  $\text{CO}$ . In general, the phenyl olefine ketones formed from mixed ketones have a straight C-chain if caustic soda is used as the condensing agent, but a branched chain if hydrogen chloride is used (Harries, Ber. 35, 3088; Stoermer, Ber. 35, 3549). With an excess of benzaldehyde, dibenzylidene ketones are formed:



For colour reactions of  $\alpha,\beta$ -unsaturated ketones, see Reddelien, Ber. 45, 2904.

Benzylidene-acetone, benzal-acetone, styryl-methyl ketone,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_3$ , m.p.  $41^\circ$ , b.p.  $262^\circ$ , is obtained by the distillation of a mixture of calcium cinnamate and acetate; by the condensation of benzaldehyde and acetone with dilute caustic soda as condensing agent (Claisen, Ann. 223, 139); from styrene and acetyl chloride by means of stannic chloride, when an addition product is formed from which hydrogen chloride is removed by means of diethyl-aniline (Langlois, C.r. 168, 1052); by the hydrogenation of *sym*-acetylphenyl-acetylene,  $\text{C}_6\text{H}_5\text{C}:\text{C}\cdot\text{COCH}_3$ , and in small quantities by the action of methyl magnesium iodide on cinnamionitrile (Kohler, Am. Ch. J. 35, 386).

It dissolves in sulphuric acid with an orange-red colour. With mercaptans it combines to give mercaptols, and these add on a third molecule of mercaptan to the olefine linkage:  $\text{C}_6\text{H}_5\text{CH}(\text{SR})\text{CH}_2\text{C}(\text{SR})_2\text{CH}_3$  (Posner, Ber. 35, 804). With alcoholic ammonium sulphide, it gives a dimeric benzylidene-thioacetone,  $(\text{C}_{10}\text{H}_{10}\text{S})_2$ , m.p.  $132^\circ$ , which gives beautifully crystallising addition products with water, acids, and salts (Fromm, Ber. 40, 2982). Benzylidene-acetone-phenylhydrazone,

m.p. 158°, readily changes to 1,6-diphenyl-3-methyl-pyrazoline (Knorr, Ber. 20, 1099). Oxime, m.p. 115° (Zelinsky, Ber. 20, 923). Its oxide exists in two forms, one melting at 53°, and the other a liquid (Ger. Pat. 395,435). On boiling with sodium hypochlorite, benzylidene-acetone decomposes into chloroform and cinnamic acid. On reduction, benzylacetone, and diphenyl-octudione, are formed, the latter being produced by the union of two molecules of the olefine-ketone. The homologues of benzylidene-acetone seem to behave similarly (Harries, Ber. 35, 968, 3089). For its progressive catalytic reduction to phenyl- and hexahydrophenyl-butanol, see C. 1912, II, 519. Benzal-acetoxime is reduced by sodium and alcohol to 1-phenyl-3-aminobutane,  $C_6H_5CH_2CH_2(NH_2)CH_3$ , but zinc dust and acetic acid only reduce it to 1-phenyl-3-aminobutene,  $C_6H_5CH:CHCH(NH_2)CH_3$ . The latter is decomposed by ozone into benzaldehyde and  $\alpha$ -amino-propionaldehyde (Harries, Ber. 36, 2997; 37, 615). On nitration, *o*- and *p*-nitrobenzylidene-acetones, m.p. 60° and 110°, are formed. *o*-Nitrobenzal-acetone is readily converted into indigo. On reduction it forms quinaldine, with elimination of water (Vol. IV).

*p*-Aminobenzylidene-acetone, m.p. 81°, and *p*-dimethylamino-benzylidene-acetone, m.p. 132°, are obtained by condensing amino- and dimethylamino-benzaldehydes with acetone. They dissolve in hydrochloric acid with a red and yellow colour, respectively, and wool, silk, and cotton, mordanted with tannic acid, are dyed by these solutions.

$\alpha$ - and  $\gamma$ -Benzylidene-methyl-ethyl-ketones,  $C_6H_5CH:CHCOCH_2H_5$ , m.p. 39°, and b.p. 142° (12 mm.), and  $C_6H_5CH:C(CH_3)COCH_2H_5$ , m.p. 38°, b.p. 127-130° (12 mm.), and  $\alpha$ - and  $\gamma$ -benzylidene-methyl-propyl ketones,  $C_6H_5CH:CHCOCH_2C_2H_5$ , b.p. 155° (20 mm.), and  $C_6H_5CH:C(CH_3)COCH_2C_2H_5$ , b.p. 120° (18 mm.), are obtained from benzaldehyde and methyl-ethyl- and methyl-propyl-ketones, respectively, using caustic soda or hydrogen chloride as condensing agent. On the other hand, benzaldehyde and phenoxy-acetone with either sodium hydroxide or hydrogen chloride give  $\alpha$ -benzylidene-phenoxy-acetone,  $C_6H_5CH:C(OC_6H_5)COCH_3$ , m.p. 102°, which undergoes a degradation to  $\alpha$ -phenoxy-cinnamic acid (p. 484) when treated with alkali hypochlorites (Stoermer, Ber. 35, 3549).

Cuminal-acetone (Claisen, Ann. 223, 147). Benzylidene-pinacoline,  $C_6H_5CH:CH:COC(CH_3)_2$ , m.p. 41°, b.p. 154° (25 mm.), is obtained from benzaldehyde and pinacoline. It adds on malonic ester with formation of a  $\delta$ -keto-acid (Vorländer, Ber. 30, 2268).

Phenyl-vinyl-ketone,  $C_6H_5COCH:CH_2$ , b.p. 115° (18 mm.), is a colourless oil with a pungent smell. It is obtained (1) by the action of an alcoholic solution of potassium iodide on  $\alpha,\beta$ -dibromo-propiophenone; (2) from benzoyl chloride ethylene oxide, and aluminium chloride (Norris, Am. 42, 2392); (3) from phenyl-propargyl alcohol (p. 457) by rearrangement with mercuric acetate and acetic acid (Venus-Danilova, Zh. 2, 645); (4) by the distillation of triphenacyl-methylamine hydrochloride (p. 406) with steam (Schäfer, Ber. 39, 2187). Its dimethyl-acetal is formed from cinnamic aldehyde and sodium methylate, when, as a matter of fact, the acetal of cinnamic aldehyde would be expected (Straus, Ann. 401, 121). In sunlight, or on heating, it readily polymerises. With aluminium chloride it isomerises to  $\alpha$ -hydrindone. It readily combines with hydrogen chloride, alcohol, and sodium bisulphite, the double bond being opened. With phenyl-hydrazine it gives 1,3-diphenyl-pyrazoline (Kohler, Am. Ch. J. 42, 375). *o*-Nitrostyryl-phenyl ketone,  $C_6H_5COCH:CHC_6H_4(2)NO_2$ , m.p. 122-123°, is obtained from *o*-nitrobenzaldehyde and acetophenone using gaseous hydrogen chloride as condensing agent. It gives 2-phenyl-quinaldine (Vol. IV), on boiling with alcoholic hydrogen chloride.

Phenyl-propenyl ketone,  $C_6H_5COCH:CH\cdot CH_3$ , m.p. 20-21°, b.p. 135° (20 mm.), can be obtained from crotonyl chloride, benzene, and aluminium chloride, and from dibromo-butyrophenone, by the action of potassium iodide (Kohler, Am. Ch. J. 42, 375).

Allyl-acetophenone,  $C_6H_5CO\cdot CH_2\cdot CH_2\cdot CH:CH_2$ , b.p. 236°, is obtained from allyl-benzoyl-acetic acid (Baeyer, Ber. 16, 2132; Heller, Ann. ch. [10], 2, 269).

#### 4b. Hydroxyphenyl Olefine Ketones

For the condensation of hydroxy-aldehydes with acetone, see Glaser, J. pr. 116, 331. *o*-Hydroxy-benzylidene-acetone,  $HO\cdot C_6H_4CH:CH\cdot COCH_3$ , m.p. 139°,

is obtained from salicylaldehyde and acetone, or by the action of emulsin on glyco-methyl-*o*-coumar-ketone,  $C_6H_{11}O_6 \cdot O \cdot C_6H_4CH:CH \cdot COCH_3$ , m.p.  $192^\circ$ , the condensation product of helicin and acetone (*Harries*, Ber. 24, 3130). For homologous *o*-hydroxy-olefine ketones, see *McGookin*, J. 127, 2539. *m*-Methoxybenzylidene-acetone, b.p.  $173^\circ$  (8 mm.) (*Bauer*, J. pr. 88, 329). *p*-Hydroxybenzylidene-acetone, m.p.  $103^\circ$ , is obtained from *p*-hydroxy-benzaldehyde, acetone, and hydrogen chloride, but the principal product of the reaction is *p,p*-dihydroxy-dibenzylidene-acetone (*Zincke*, Ber. 36, 134). *o*-, *m*-, and *p*-Hydroxybenzylidene-acetone-*o*-acetic acids, m.p.  $108^\circ$ ,  $122^\circ$ , and  $177^\circ$  (*Elkan*, Ber. 19, 3056). Vanillylidene-, isovanillylidene-, veratrylidene-, piperonylidene-acetones, m.p.  $130^\circ$ ,  $92-93^\circ$ ,  $91-92^\circ$ ,  $107-108^\circ$  (*Kaufmann*, Ber. 49, 678). 4-Hydroxy-3-methoxy-phenethyl-*n*- $\Delta^1$ -heptenyl ketone, *shogaol*,  $HO[4]CH_2O[3]C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH:CHC_6H_{11}$ , b. p.  $201-203^\circ$  (2-2.5 mm.), is together with zingerone (p. 353) the essential principle of ginger. It has been synthesised from zingerone by the action on *n*-caproic aldehyde, the OH group being protected during the reaction (*Nomura*, Rep. Tohoku, 7, 67; Proc. Tokyo, 3, 159). 3,4-Methylene-dioxy-hydrocinnamylidene-acetone,  $CH_2O_2[3,4]C_6H_3CH_2CH_2CH:CHCOCH_3$ , dinitrophenyl-hydrazone, m.p.  $147-148^\circ$ , has been prepared from kawa methysticin (*Borsche*, Ber. 62, 360).

### 5. Phenyl-acetylene Aldehydes

Phenyl-propargaldehyde,  $C_6H_5C:C \cdot CHO$ , b.p.  $128^\circ$  (28 mm.), is prepared from sodio-phenylacetylene by the action of ethyl formate in ether (*Charon*, C.r. 137, 125), or better from its acetal. The latter is readily obtained from the acetal of  $\alpha$ -bromo-cinnamic aldehyde (p. 458) or from phenyl-acetylene magnesium bromide with orthoformic ester, and gives the aldehyde on treatment with dilute acids. Phenyl-propargaldehyde is decomposed into phenyl-acetylene and formic acid by aqueous alkalis even in the cold. Its oxime,  $C_6H_5C:C \cdot CH:NOH$ , m.p.  $108^\circ$ , isomerises under the influence of aqueous alkalis to phenyl-isoxazole, and with sodium ethylate further to  $\omega$ -cyanoacetophenone,  $C_6H_5CO \cdot CH_2 \cdot CN$  (*Claisen*, Ber. 36, 3670). It gives two stereoisomeric semicarbazones; an unstable form m.p.  $193^\circ$ , and a stable form m.p.  $132-134^\circ$  (*Auwers*, Ber. 58, 2080).

### 6. Phenyl-acetylene ketones

These have been synthesised from sodio-phenylacetylene by the action of the esters, chlorides, and anhydrides of acids (*Moureu*, C.r. 134, 45). Acetyl-phenyl-acetylene,  $C_6H_5C:CCOCH_3$ , b.p.  $130^\circ$  (22 mm.), gives benzoyl-acetone when treated with sulphuric acid, and is decomposed by caustic potash into phenyl-acetylene and acetic acid. Butyryl-phenyl-acetylene,  $C_6H_5COC:CC_6H_5$ , m.p.  $136^\circ$  (9 mm.). Benzoyl-amyl-acetylene,  $C_6H_5COC:CC_6H_{11}$ , b.p.  $178^\circ$  (19 mm.), gives benzoyl-caproyl-methane with dilute sulphuric acid. With primary and secondary amines phenyl-acetylene ketones combine to form  $\beta$ -substituted ethylene-amino ketones,  $Ar \cdot C(NHR):CH \cdot CO \cdot Alk$ , which give  $\beta$ -diketones when hydrolysed (*André*, C.r. 152, 1488).

### 7. Phenyl Diolefine Ketones

The aryl-olefine ketones,  $Ar(CH:CH)_nCO \cdot Alk$ , tend to resinify (*Herzog*, Z. angew. 35, 641). Cinnamylidene-acetone,  $C_6H_5 \cdot CH:CH \cdot CH:CH \cdot COCH_3$ , m.p.  $68^\circ$ , has been obtained from kawaic acid (p. 485) by heating with dilute sulphuric acid (*Borsche*, Ber. 62, 371), and by condensing cinnamic aldehyde and acetone. Its oxime gives a pyridine derivative when dry distilled. 3,4-Methylene-dioxy-cinnamylidene-acetone, "piperonylidene-acetone," methysticon,  $(CH_2O_2)_2C_6H_3 \cdot CH:CH \cdot CH:CH \cdot CO \cdot CH_3$ , m.p.  $89^\circ$  (*Scholtz*, Ber. 28, 1193; 29, 613). Benzylidene-mesityl oxide,  $C_6H_5 \cdot CH:CH \cdot CO \cdot CH:C(CH_3)_2$ , b.p.  $178^\circ$  (14 mm.) (*Claisen*, Ber. 14, 351).

### 8. Phenyl Olefine Diketones

Benzylidene-diacetyl,  $C_6H_5CH:CHCOCOCH_3$ , forms yellow leaflets, m.p.  $52-53^\circ$ . It is obtained from diacetyl-monophenylhydrazone and benzaldehyde,

the condensation product being decomposed with dilute sulphuric acid (*Diels*, Ber. 44, 883). Cinnamoyl-acetone,  $C_6H_5CH:CHCOCH_2COCH_3$ , pale-yellow needles, m.p.  $83-81^\circ$ , is obtained from methyl cinnamate, acetone and sodium. As it dissolves in aqueous potash, it may possess an enolic structure (*Ryan*, Proc. Irish Ac., 32).

### 9. Phenyl Diolefine Diketones

$\alpha$ -Cinnamylidene-acetylacetone,  $C_6H_5CH:CHCH:CHCOCH_2COCH_3$ , m.p.  $139-140^\circ$ , is obtained from ethyl cinnamylidene-acetylacetoacetate (p. 487), the condensation product of cinnamylidene-acetyl chloride and sodio-acetoacetic methyl ester, which is heated with water at  $130^\circ$  (*Borsche*, Ber. 60, 1137). Its *p*-methoxy derivative, yangonol, m.p.  $93^\circ$ , is obtained from yangonin, a pyrone derivative found in kawa resin, which, when decomposed by alkali, gives a  $\beta,\delta$ -diketo-carboxylic acid, yangonoic acid. This gives yangonol by loss of carbon dioxide. It has been synthesised, starting from *p*-methoxy-cinnamylidene-acetyl chloride, which is combined with sodio-acetoacetic ester, and treated as above (*Borsche*, Ber. 60, 2112).

### 10. Phenyl Olefine Carboxylic Acids

Two classes of phenyl olefine carboxylic acids may be distinguished. One class is derived from saturated benzene-carboxylic acids, a hydrogen atom of the ring being replaced by an unsaturated side-chain, of which vinyl-benzoic acid is an example. The other class comprises the phenylated olefine monocarboxylic acids.

**A. PHENYL OLEFINE CARBOXYLIC ACIDS in which the COOH group is attached (1) to the ring, or (2) to a saturated side-chain.** (1) *o*-Vinyl-benzoic acid,  $CH_2:CH[C_6H_4COOH]$ . *o*-Vinyl-benzoic acids, chlorinated in the vinyl and in the phenyl residu, have been obtained as decomposition products of chloro-derivatives of hydrindene and naphthoquinone (*Zincke*, Ber. 27, 2761; *Wislicenus*, Ann. 275, 347). *m*-Vinyl-benzoic acid, m.p.  $95^\circ$ , has been obtained from *m*-amino-styrene (*Komppa*, Ber. 26, R 677). *p*-Allyl-benzoic acid,  $CH_2:CHCH_2 \cdot C_6H_4COOH$ , m.p.  $104-105^\circ$ , is obtained from the magnesium compound of *p*-bromo-allyl-benzene by the action of carbon dioxide. (*Quelet*, Bull. 45, 255). *o*-, *m*-, and *p*-Isopropenyl-benzoic acids,  $CH_2:C(CH_3) \cdot C_6H_4COOH$ , melt at  $60^\circ$ ,  $90^\circ$ , and  $101^\circ$  (*Meyer*, Ann. 219, 270; *Kothe*, Ann. 248, 64; *Wallach*, Ann. 275, 160).

(2) *o*-Vinyl-phenyl-acetic acid,  $CH_2:CH \cdot C_6H_4 \cdot CH_2 \cdot COOH$ . Derivatives of this acid in which the vinyl residue is chlorinated have also been obtained by the decomposition of chlorinated keto-hydronaphthalenes (*Zincke*, Ber. 21, 3555).

**B. PHENYL OLEFINE CARBOXYLIC ACIDS in which the carboxyl group is attached to an unsaturated side-chain.** True phenyl olefine monocarboxylic acids can be obtained by the oxidation of the corresponding alcohols and aldehydes, in the same way as olefine carboxylic acids are prepared from the paraffin monocarboxylic or fatty acids (Vol. I, p. 337). There is, however, a synthetic reaction of much greater importance, known as Perkin's synthesis, which consists in allowing the sodium salt of a fatty acid and the anhydride of the acid to react with an aromatic aldehyde.

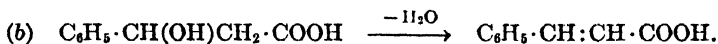
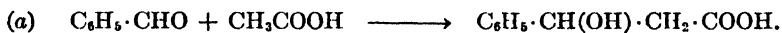
*History*.—As early as 1856, *Bertagnini* had stated that cinnamic acid was formed when benzaldehyde was heated with acetyl chloride. *W. H. Perkin, Sr.*, in 1865, succeeded in synthesising coumarin, the lactone of *o*-hydroxy-cinnamic acid (p. 472) by heating sodio-salicylaldehyde with acetic anhydride. In 1875, *W. H. Perkin* varied this reaction by allowing sodium acetate and acetic anhydride to act on salicylaldehyde. In this form Perkin's reaction has proved to be of extraordinarily wide application. It is, indeed, one of the most fruitful nuclear-

synthetic reactions known, and a great number of chemists have contributed to its development. The mechanism of the reaction has been studied by *Baeyer* and *Jackson*, *Conrad* and *Bischoff*, *Oglialoro*, and especially by *Fillig* and his pupils, *Jayne* and *Slocum* (Ann. 227, 48). It has been found that:

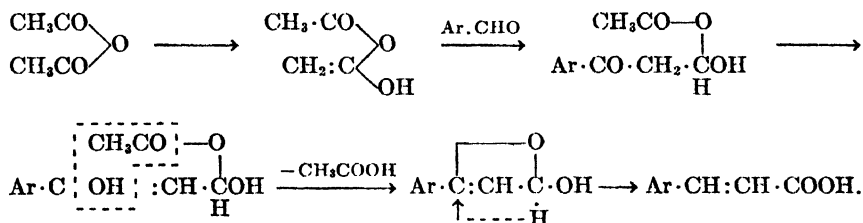
1. When an aromatic aldehyde condenses with a fatty acid, the carbon atom linked to the carboxyl group links itself to the carbon of the aldehyde group.

2. The question of whether the aldehyde reacts with the sodium salt, or with the anhydride of the aliphatic acid is still open. If the anhydride of one and the sodium salt of another acid are used, as a rule the mixtures of the two possible phenyl olefine carboxylic acids are obtained, the composition of the mixture varying with the conditions (*Michael*, Ber. 34, 918).

3. Two phases of the condensation can be distinguished: (a) the aldehyde and the acid combine additively, as in the aldol reaction, to form a  $\beta$ -hydroxy-acid; and (b) this  $\beta$ -hydroxy-acid loses water, and an olefine carboxylic acid is formed. In some cases the first phase of the reaction has been fixed:

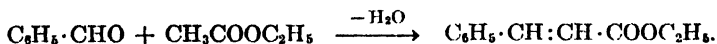


The yield of unsaturated acid is greatly increased in the presence of pyridine (*Bacharach*, Am. 50, 3333; U. S. Pat. 1,853,030), and if pyridine is used the sodium acetate can be dispensed with. Other tertiary bases are equally effective, and the explanation has been offered that they enolise the acid anhydride and thus enable it to add on to the aromatic aldehyde; further, the addition product is enolised and the acid is thus liberated. Hence the reaction would consist of the following stages: (1) the acid anhydride enolises; (2) the aldehyde adds on to this enol; (3) the addition product enolises; (4) the acid is liberated from the enol; and (5) the residual molecule changes to an unsaturated acid (*Kalnin*, Helv. 11, 977):



For the theory of Perkin's reaction see also *Muller*, Ann. 491, 251; *Kuhn*, Ber. 64, 2347; *Kalnin*, *ibid.*, 2935; *Brodski*, Zh. 2, 814.

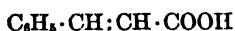
Another synthetic method of making the phenyl olefine carboxylic acids is due to *Claisen* (Ber. 23, 976; see *Stoermer*, Ber. 36, 1933; *Scheibler*, Ann. 445, 141; *Marvel*, Org. Synth. 9, 38). It consists in condensing aromatic aldehydes and aliphatic esters by means of sodium ethoxide or sodium:



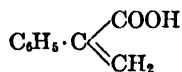
Another method, originally worked out for aliphatic compounds, consists in condensing aromatic aldehydes and acids or esters with a reactive  $CH_2$  group, such as malonic acid and its esters, acetoacetic ester, *etc.*, using ammonia, or primary, secondary, or tertiary bases as condensing agents. If malonic acid is used, carbon dioxide splits off in the course of the condensation, and unsaturated monobasic acids are formed directly (*Knoevenagel*, Ber. 32, 2596; 33, 2140).



**PHENYL-ACRYLIC ACIDS.** Theory indicates the existence of two isomerides,  $\alpha$ - and  $\beta$ -phenyl-acrylic acids. They are also known as cinnamic and atropic acids:



$\beta$ -Phenyl-acrylic acid  
or cinnamic acid



$\alpha$ -Phenyl-acrylic acid  
or atropic acid

**Cinnamic acid,  $\beta$ -phenyl-acrylic acid,**  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{COOH}$  (for its steric formula, see p. 465), m.p. (*trans*-form)  $133^\circ$ , b.p.  $300^\circ$ , occurs in balsam of Peru, and balsam of tolu, in storax (see cinnamyl alcohol, p. 456) and in certain benzoin resins. Together with  $\alpha$ - and  $\beta$ -truxillic and allo-cinnamic acids it is found among the acids formed in the decomposition of the cocaine alkaloids.

**Methods of formation:**—Cinnamic acid is obtained: (1) by the oxidation of its alcohol and aldehyde; (2) by the reduction of phenyl-propionic acid with zinc and acetic acid (Aronstein, Ber. 22, 1181); (3) by nuclear synthesis from sodium acetate, acetic anhydride and benzaldehyde (Perkin's synthesis) or from benzaldehyde and ethyl acetate and sodium ethylate (see above); (4) by heating benzylidene chloride with sodium acetate (this reaction has been used industrially); (5) from benzylidene-malonic acid (p. 488) by the action of heat; (6) its phenyl ester is obtained by heating phenyl-fumarate (p. 197). Cinnamic acid is also obtained (7) from synthetic  $\beta$ -phenyl-hydracrylic acid by loss of water; and (8) industrially by the action of sodium hypochlorite on benzylidene-acetone (Schorygin, Zh. 1, 506).

Phenyl-propionic acid gives *trans*-cinnamic acid when reduced with sodium and alcohol, or zinc and acetic acid, but the *cis*-acid almost entirely on catalytic reduction (Paal, Ber. 42, 3931; Fischer, Ann. 386, 380).

**Properties and reactions:**—Cinnamic acid crystallises in slender needles from hot water, and in thick prisms from alcohol. There are two crystalline modifications: the  $\alpha$ -form is diamond-shaped and stable, and the  $\beta$ -form is needle-like, and unstable. Both have the same m.p.,  $133^\circ$ , and are mutually convertible (Stobbe, Ber. 58, 2415; de Jong, Rec. 49, 216). It dissolves in 3500 parts of water at  $17^\circ$ , and readily in hot water. It can be purified by distillation in a good vacuum, or by crystallisation from petroleum benzine (Miller, Ann. 188, 194). The cinnamates give a yellow precipitate with ferric chloride.

Several compounds of cinnamic acid are used as drugs in the treatment of tuberculosis.

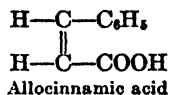
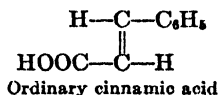
On oxidation with nitric or chromic acid, cinnamic acid gives benzaldehyde and benzoic acid, and with permanganate it gives phenyl-glycerolic acid, m.p.  $141^\circ$  (p. 419). It breaks down into benzoic and acetic acids when fused with potash. As an unsaturated acid it readily adds on hydrogen, hydroxylamine, hydrogen bromide and iodide, bromine, chlorine, and hypochlorous acid, with the formation of hydrocinnamic acid (p. 294),  $\beta$ -hydroxylamino-,  $\beta$ -bromo-,  $\beta$ -iodo-hydrocinnamic acids (p. 418), phenyl  $\alpha, \beta$ -dichloro- and phenyl  $\alpha, \beta$ -dibromo-propionic acids, the dichloride and dibromide of cinnamic acid, and  $\beta$ -phenyl- $\alpha$ -chloro-lactic acid (p. 420). Cinnamic acid reacts with normal and acid sulphites, adding on  $\text{NaHSO}_3$  across the double bond, and forming sulphonates (Bougault, C.r. 156, 396).

**Derivatives of cinnamic acid.** Its methyl ester, m.p.  $33^\circ$ , b.p.  $263^\circ$ , occurs in various essential oils. Ethyl ester, *cis*- m.p.  $90^\circ$ , b.p.  $125^\circ$  (12 mm.); *trans*- m.p.  $91^\circ$ , b.p.  $142^\circ$  (12 mm.) (Auwers, J. pr. 84, 84). Phenyl ester, m.p.  $72^\circ$ , m.p.  $72^\circ$ , b.p.  $206^\circ$  (15 mm.), see cinnamic acid. Catechol ester, m.p.  $129^\circ$  (Anschütz, Ber. 11, 1220; 18, 1945; Hartmann, Ber. 25, 3533). Guaiacol ester, styracole, m.p.  $142^\circ$  (Angeletti, Giorn. Farm. 82, 361). Benzyl ester, m.p.  $30^\circ$ , found in the oil of Balsam of Peru (Kraut, Ber. 2, 180). Styryl ester, styracin,

m.p. 14°. Chloride, m.p. 35°, b.p. 154° (25 mm.). Anhydride, m.p. 130° (*Liebermann*, Ber. 27, 284). Amide, m.p. 142°. Anilide, m.p. 151°. The nitrile is obtained from benzaldehyde and cyanoacetic acid with pyridine as condensing agent, the product being heated to remove carbon dioxide. It is known in two stereoisomeric forms: *cis*- m.p. -13°, b.p. 115° (12 mm.); and *trans*- m.p. 23°, b.p. 129° (12 mm.) (*Ghosez*, Belg. 41, 477). *Dicinnamoyl peroxide*, m.p. 133° (decomp.), is prepared from cinnamyl chloride and alcoholic hydrogen peroxide. It gives *percinnamic acid*,  $C_6H_5CH:CH \cdot CO_2H$ , with sodium ethylate (*Bodendorf*, Ber. 66, 165).

### Unstable and Polymorphous Modifications of Cinnamic Acid

Like the  $\beta$ -alkyl-acrylic acid (Vol. I, p. 343), the  $\beta$ -phenyl-acrylic acids are known in stable and unstable stereoisomeric forms. The latter are called **allocinnamic acids**. Allocinnamic acid itself has the very remarkable property of existing in four chemically identical but crystallographically different forms, which are interconvertible by simply melting and crystallising (*Bülmann*, Ber. 42, 182, 1443). Their m.p. are 32° (*Weygand*, Ber. 65, 694), 42° (*Erlenmeyer's* isocinnamic acid), 58° (*Liebermann's* isocinnamic acid), and 68° (*Liebermann's* allocinnamic acid by the older nomenclature). The acid of m.p. 32° is the least stable of them all. It is obtained from the melt and has a life period of only a few minutes. The acid of m.p. 42° is also unstable. With certain precautions it can be obtained from the melt and from the solution of all three acids, and also by precipitating the solutions of cinnamates with acids (*Liebermann*, Ber. 42, 4659; 43, 411). It is the primary product in any reaction giving rise to the allocinnamic acids. It is very readily converted into the latter, particularly the most stable of them (m.p. 68°), *e.g.*, by contact with the smallest trace of a crystal of them. Allocinnamic acid, in one or other of the three relatively stable forms, obtained: (1) by the partial reduction of phenyl-propionic acid (p. 478) with hydrogen and colloidal palladium (*Paal*, Ber. 42, 3930); (2) by the reduction of *allo- $\alpha$* - and *- $\beta$* -bromocinnamic acids with zinc dust and alcohol; (3) by exposing a solution of ordinary cinnamic acid to ultraviolet rays (*Stoermer*, Ber. 42, 4869); and (4) together with a good deal of ordinary cinnamic acid by heating benzylidene-malonic acid. The acid of m.p. 58° was first detected among the decomposition products of the cocaine alkaloids, ordinary cinnamic acid being also present. Allocinnamic acid, m.p. 68°, forms an aniline salt, m.p. 83°, which is sparingly soluble in ligroin. Its addition products with chlorine and bromine, *allocinnamic dichloride* and *dibromide* (p. 420) are different from those obtained with ordinary cinnamic acid. It is converted into ordinary cinnamic acid by distillation at ordinary pressure, or by the action of conc. sulphuric acid, or by irradiation in benzene in the presence of a little iodine. It is oxidised by permanganate to phenyl-glycerolic acid, m.p. 122° (p. 419). It reacts differently from ordinary cinnamic acid with fuming sulphuric acid. It loses water and readily polymerises to *truxone* (*Liebermann*, Ber. 28, 1446; 31, 2095). These reactions of allocinnamic acid, and especially its formation from phenyl-propionic acid and  $\beta$ -bromo-allocinnamic acid, are regarded as evidence for assigning a maleinoid or *cis*-structure to  $\beta$ -phenylacrylic acid. Ordinary cinnamic acid must therefore be the fumaroid or *trans*-form:



This view is also supported by evidence drawn from the behaviour of the *o*-hydroxy-cinnamic acids (p. 473) whose steric configuration can be deduced from their different tendency to lose water; also by the fact that allocinnamic acid

forms an addition product with mercury salts,  $C_6H_5CH(OH)CHHg \cdot COO$ , while cinnamic acid fails to do so. Observations with other *cis-trans* isomeric olefine dicarboxylic acids (*Bülmann*, Ber. 43, 568) seem to show that this reaction is peculiar to the maleinoid forms.

The heat of combustion of *cis*-cinnamic acid, m.p. 68°, is 1048 kcal. and that

of the *trans*-acid is 1041 kcal. The dissociation constants are 0.0138 and 0.00355, respectively.

The view that the allocinnamic acids were polymorphous and chemically identical has been particularly advocated by *de Jong* (Rec. 48, 1098; 49, 216), because the three allocinnamic acids known at that time were found to form one and the same double compound, the so-called "triclinic double-salt" with ordinary (*trans*) cinnamic acid. This view has been challenged by *Stobbe* (Ann. 402, 187; Ber. 58, 2859), who found the solutions and melts and their mixtures to show differences, and has investigated the systems solid/liquid and solid/solid. On this evidence he bases the view that the 68° acid is monomorphous and chemically isomeric with the acids of m.p. 58° and 42°. The former is always homogeneous, while the latter two are mixtures of two or three acids. These are chemically different from each other as well as from the ordinary acid m.p. 133°. This view is also supported by the fact that bromine is added on by the different allocinnamic acids at different rates (*Meyer*, Z. physik. Ch. 145, 360; cf., however, *Robinson*, J. 1933, 1453). *Weygand* (Ber. 65, 695) has studied the behaviour of the four acids under the polarisation microscope, and the rate of their mutual conversions, and he also criticises *de Jong's* proof of polymorphism.

When exposed to light, solid ordinary cinnamic acid dimerises to  $\alpha$ -truxillic acid, and allocinnamic acid to  $\beta$ -truxic acid (Vol. II, p. 41). The  $\alpha$ -acid occurs together with  $\beta$ -,  $\gamma$ -, and  $\delta$ -truxillic acids in the cocaine alkaloids. On distillation, both these dimeric acids give ordinary cinnamic acid, but on irradiation with short-wave ultra-violet light each of them regenerates the acid from which it was formed. It is noteworthy that the change of cinnamic to truxillic acid does not imply any change of energy; the heat of combustion of the two acids is the same (*Rüder*, Z. physik. Ch. A, 48, 345).

### Cinnamic Acids Substituted in the Side-chain

(a) *Phenyl-monohalogeno-acrylic acids*. Although structural theory predicts the existence of two isomeric phenyl-monochloro-acrylic acids, in fact, each of these structural isomers is known in two stereo-isomeric modifications (see above). They are usually distinguished as  $\alpha$ - and  $\beta$ -chloro-cinnamic and allo- $\alpha$ - and - $\beta$ -chlorocinnamic acids (*Michael*, J. pr. 40, 63; *Erlenmeyer*, Ann. 287, 1). For their interconversions on irradiation, see *Stoermer*, Ber. 46, 1249; for the separation of the stereoisomeric  $\alpha$ -halogeno-cinnamic acids, see *Bougault*, Bull. 21, 172.

$\alpha$ -Fluoro-cinnamic acid,  $C_6H_5CH:CF \cdot COOH$ , m.p. 157.6°, is obtained by the action of benzaldehyde on fluoro-acetic acid (*Swarts*, Bull. 25, 325).

$\alpha$ -Chloro-cinnamic acid,  $C_6H_5 \cdot CH:CCl \cdot COOH$ , m.p. 139°, is obtained (1) from phenyl- $\alpha, \beta$ -dichloropropionic acid by the action of alcoholic potash; (2) from benzaldehyde by the action of sodium monochloroacetate and acetic anhydride; (3) from phenyl- $\alpha$ -chlorolactic acid by the action of sodium acetate and acetic anhydride; and (4) from its aldehyde by oxidation with chromic oxide,  $CrO_3$  (*Naar*, Ber. 24, 249). Allo- $\alpha$ -chloro-cinnamic acid, m.p. 112-114°, is obtained as a by-product in method (1).  $\beta$ -Chloro-cinnamic acid,  $C_6H_5 \cdot CCl:CH \cdot COOH$ , m.p. 142°, and allo- $\beta$ -chloro-cinnamic acid, b.p. 132.5°, are obtained by the addition of hydrogen chloride to phenyl-propionic acid.

$\alpha$ -Bromo-cinnamic acid,  $C_6H_5 \cdot CH:CBBr \cdot COOH$ , m.p. 131°, and allo- $\alpha$ -bromo-cinnamic acid, m.p. 120° (Glaser's  $\beta$ -bromo-cinnamic acid), are obtained from phenyl- $\alpha, \beta$ -dibromo-propionic acid by the action of alcoholic potash (*Sudborough*, J. 83, 666). The second of these compounds is converted on heating into  $\alpha$ -bromo-cinnamic acid (which has a higher m.p.), and by reduction with zinc dust and alcohol gives allocinnamic acid. On oxidation, both acids give benzaldehyde.  $\beta$ -Bromo-cinnamic acid,  $C_6H_5CBBr:CH \cdot COOH$ , m.p. 135°, and allo- $\beta$ -bromo-cinnamic acid, m.p. 160°, are formed together when phenyl-propionic acid adds on hydrogen bromide. The allo-acid changes to  $\beta$ -bromo-cinnamic acid on heating, which is in this case the lower melting isomer. On reduction the allo-acid gives both cinnamic and allocinnamic acids.

$\alpha$ -Iodo-cinnamic acid,  $C_6H_5CH:CI \cdot COOH$ , m.p. 162-163°, white leaflets, and allo- $\alpha$ -iodo-cinnamic acid, m.p. 110-111°, are obtained from phenyl-pyruvic acid by the action of iodine and potassium iodide in caustic soda (*Bougault*, Bull. 21, 46). For  $\alpha$ -cyano-cinnamic acid, m.p. 183°, and other  $\beta$ -aryl- $\alpha$ -cyano-acrylic

acids, which are obtained from cyanoacetic acid and aromatic aldehydes, see Arch. Pharm. 271, 294.

(b) *Phenyl-dihalogeno-acrylic acids*. These are obtained by adding on the halogens to phenyl-propionic acid, *cis*- $\alpha,\beta$ -dichloro-cinnamic acid,  $C_6H_5 \cdot CCl_2 \cdot COOH$ , m.p. 121°; *trans*-acid, m.p. 101°. *cis*- and *trans*- $\alpha,\beta$ -Dibromo-cinnamic acids, m.p. 100° and 136°. *cis*- and *trans*- $\alpha,\beta$ -Diiodo-cinnamic acids, m.p. 121° and 171° (Stoermer, Ber. 46, 1249). Ethyl  $\alpha,\beta$ -dinitro-cinnamate is obtained from ethyl phenyl-propionate by the action of nitrogen peroxide at 0°; it exists in an oily form, thought to be the *cis*-compound, and a solid form, m.p. 66°, which would be the *trans*-form (Wieland, Ber. 53, 1343).  $\alpha$ - and  $\beta$ -Sulphydryl-cinnamic acids,  $C_6H_5CH:C(SH)COOH$  and  $C_6H_5C(SH):CHCOOH$ , m.p. 179° and 110°, have been prepared from benzylidene-thiocyanic acid,  $C_6H_5CH:C(SH) \cdot CO \cdot SCN$  (Ginsburg, Ber. 19, 123), and from the addition product of phenyl-propionic acid and thiourea (Fischer, Ber. 47, 2469).

(c)  $\alpha$ -Amino-cinnamic acid,  $C_6H_5 \cdot CH:C(NH_2) \cdot COOH$ , decomposes at 240–250° when rapidly heated, phenyl-vinylamine being formed. Its hydrochloride is obtained from benzoyl-amino-cinnamic azlactone (see below) by the action of hydrogen chloride at 120°, and the free acid is precipitated from the hydrochloride with sodium acetate or carbonate. The amide of an isomeric- $\alpha$ -amino acid, m.p. 160°, is formed by the action of ammonia on phenyl-dibromo-propionic or  $\alpha$ -bromo-cinnamic esters (Baucke, Rec. 15, 128). The formula given above is uncertain. Possibly the desmotropic formulation as a phenyl-pyruvic imide,  $C_6H_5 \cdot CH_2 \cdot C(NH)COOH$ , is better for both  $\alpha$ -amino-cinnamic acid itself and its derivatives.

$\alpha$ -Acetamino-cinnamic acid,  $C_6H_5 \cdot CH:C(NHCOCH_3) \cdot COOH + 2H_2O$ , m.p. 190° (anhydrous; decomp.), is obtained by the action of caustic soda on its az-



lactone.  $\alpha$ -Acetamino-cinnamic azlactone,  $C_6H_5CH:C:N:CCH_3$ , m.p. 146°, is obtained by the action of acetic anhydride on phenyl- $\alpha$ -aminolactic acid, and from hippuric acid and benzaldehyde under the action of sodium acetate and acetic anhydride (p. 301).  $\alpha$ -Benzoylamino-cinnamic azlactone, m.p. 165°, is obtained by the condensation of hippuric acid and benzaldehyde with sodium acetate and acetic anhydride. When heated with dilute alkalis, it is converted into  $\alpha$ -benzoylamino-cinnamic acid,  $C_6H_5CH:C(NHCOC_6H_5)COOH$ , and this decomposes above its m.p. (225°) with the formation of phenyl-acetaldehyde, and with excess alkali breaks down into benzamide and phenyl-pyruvic acid (p. 428) (Erlenmeyer, Ber. 33, 2036). *p*-Hydroxy-benzoylamino-cinnamic azlactone, m.p. 173°, is obtained from *p*-hydroxy-benzaldehyde by the action of hippuric acid, etc.; the corresponding acid gives benzoyl-tyrosine with sodium amalgam.

### Cinnamic Acids Substituted in the Benzene Residue

These compounds are isomeric with the derivatives of cinnamic acid in which one of the substituents is in the side-chain.

(1) **MONOHALOGENO-CINNAMIC ACIDS** have been prepared from the three nitro-cinnamic acids (Gabriel, Ber. 16, 2040; Griess, Ber. 18, 961; Miersch, Ber. 25, 2109); also from *p*-chloro- and *p*-bromo-benzyl chlorides and malonic ester (Braun, Ber. 66, 1467).

*o*-, *m*-, and *p*-Chloro-cinnamic acids, m.p. 200°, 176°, and 264–265°.

*o*-, *m*-, and *p*-Bromo-cinnamic acids, m.p. 215–216°, 178°, and 249–250°.

*o*-, *m*-, and *p*-Iodo-cinnamic acids, m.p. 213°, 181°, and 255°.

(2) **NITRO-CINNAMIC ACIDS** (Wollring, Ber. 47, 108). When cinnamic acid is slowly added to nitric acid of density 1.5, *p*-nitro-cinnamic acid, and 60% of *o*-nitro-cinnamic acid are formed. These can be conveniently separated by making use of the different solubilities of their ethyl esters in alcohol, that of the *p*-acid being the less soluble. The pure esters are then hydrolysed with sodium carbonate or dilute sulphuric acid, and the acids thus obtained (Muller, Ann. 212, 122; Drewson, Ann. 212, 150; Fischer, Ann. 221, 265). The three isomeric nitro-cinnamic acids can also be prepared from the three mononitro-benzaldehydes (p. 275) by Perkin's reaction (p. 462).

*o*-, *m*-, and *p*-Nitro-cinnamic acids, m.p. 240°, 203–204°, and 286°.

*o*-, *m*-, and *p*-Ethyl nitro-cinnamates, m.p. 44°, 78°, and 133°.

**Allo-*o*-nitro-cinnamic acid**, m.p. 143°, is obtained by exposing the ordinary acid to light (*Stoermer*, Ber. 45, 3099).

On oxidation, the three nitro-cinnamic acids give the three nitro-benzaldehydes (p. 275) and the three nitro-benzoic acids (p. 319).

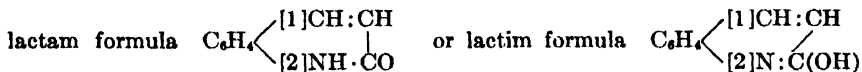
On further nitration of *o*-, *m*-, and *p*-nitro-cinnamic acids, dinitro-cinnamic acids, containing one nitro-group in the side-chain are formed (see below). ***o*,*p*-Dinitro-cinnamic acid**, (NO<sub>2</sub>)<sub>2</sub>[2,4]C<sub>6</sub>H<sub>3</sub>CH:CHCOOH, m.p. 179°, is obtained from *o*,*p*-dinitro-benzaldehyde (p. 276) by Perkin's reaction. ***m*- and *p*-Nitroso-cinnamic acids** decompose at 230° and 220° (*Awaj*, Am. Ch. J. 32, 392).

### *Cinnamic Acids Substituted both in the Benzene Nucleus and in the Side-chain*

**$\alpha$ ,*m*-Dinitro-cinnamic acid**, NO<sub>2</sub>[3]C<sub>6</sub>H<sub>4</sub>·CH:C(NO<sub>2</sub>)COOH, is obtained from ethyl-*m*-nitrocinnamate by the action of nitric and sulphuric acids, and  **$\alpha$ ,*p*-dinitro-cinnamic acid** is obtained in a similar manner from *p*-nitrocinnamic acid (*Friedländer*, Ann. 229, 224; cf. p. 445 under  $\omega$ ,*p*-dinitrophenyl-ethylene and p. 415 under *p*-amino-phenylalanine).  **$\alpha$ - and  $\beta$ -Nitro-*o*-amino-cinnamic acids**, m.p. 240° and 254°, are obtained from *o*-amino-cinnamic acid.  **$\alpha$ -Chloro-*p*-nitro-cinnamic acid**, m.p. 220–221°, is obtained from  $\alpha$ -chloro-cinnamic acid by nitration, or from *p*-nitro-dichloro-hydrocinnamic acid by boiling with pyridine. **Allo- $\alpha$ -chloro-*p*-nitro-cinnamic acid**, m.p. 153–154°.  **$\alpha$ -Chloro-*p*-amino-cinnamic acid**, turns brown at 219° without melting. It is obtained from the nitro-acid by the action of ammoniacal ferrous sulphate. **Allo- $\alpha$ -chloro-*p*-amino-cinnamic acid** forms an aceto-compound, m.p. 197–198° (*Pfeiffer*, Ber. 47, 1755). For  $\alpha$ - and  $\beta$ -bromo-*m*-nitro-cinnamic acids, see *Pfeiffer*, above, and *Reich*, Arch. Genève, 45, 191.

(3) **AMINO-CINNAMIC ACIDS** are obtained from the three mono-nitro-cinnamic acids by reduction with tin and hydrochloric acid, or better with ferrous sulphate in alkaline solution (*Gabriel*, Ber. 15, 2294; *Fischer*, Ann. 221, 266). ***o*-, *m*-, and *p*-Amino-cinnamic acids**, m.p. 158°, 181°, and 176°. The halogeno-cinnamic acids described above are obtained from their diazo-compounds by boiling with halogen acids, and *o*-, *m*-, and *p*-coumaric acids are obtained if the diazo-compounds are boiled with water. Methyl-*p*-amino-cinnamate is a local anaesthetic. For *trans*-dimethyl-amino-cinnamic acid, and the trimethyl betaine of the *trans*-*p*-amino-acid, see *Pfeiffer*, Ber. 55, 1777.

**Formation of carbostyryl**.—Unlike *o*-amino-hydrocinnamic acid, free *o*-amino-cinnamic acid does not anhydridise when heated; it behaves similarly to *o*-coumaric acid. If, however, it is heated with hydrochloric acid (*Temann*, Ber. 13, 2070) or 50% sulphuric acid (*Feer*, Ber. 18, 2395), an internal anhydride is formed. This anhydride is **carbostyryl**, discovered by *Chiozza* in 1852. He obtained it by reducing *o*-nitro-cinnamic acid with ammonium sulphide. It can be formulated either as a lactam or a lactim:



Viewed in accordance with the second formula, carbostyryl is simply *o*-hydroxy-quinoline, and it will therefore be dealt with in Vol. IV in connection with quinoline. The alkyl compounds derived from both formulae will also be dealt with in Vol. IV.

***o*-Benzoylamino-cinnamic acid**, C<sub>6</sub>H<sub>5</sub>CONH·C<sub>6</sub>H<sub>4</sub>CH:CHCOOH, m.p. 192°, is an oxidation product of *N*-benzoyl-tetrahydro-quinaldine (*Waller*, Ber. 25, 1263). ***o*-Ethylamino-cinnamic acid**, m.p. 125° (*Friedländer*, Ber. 15, 1423). Its nitrosamine, m.p. 150° (decomp.), condenses to *ethyl-isindazole-acetic acid* on reduction.

(4) ***o*-Hydrazino-cinnamic acid**, NH<sub>2</sub>NH·C<sub>6</sub>H<sub>4</sub>CH:CH·COOH, m.p. 171°, with decomposition into indazole, C<sub>6</sub>H<sub>4</sub>  $\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array}$  N (Vol. IV) and acetic acid. ***o*-**

**Sulphohydrazino-cinnamic acid**, SO<sub>3</sub>H·NH·NH·C<sub>6</sub>H<sub>4</sub>CH:CH·COOH, is obtained from *o*-diazo-cinnamic hydrochloride by the action of sodium sulphite.

With hot hydrochloric acid it breaks down into *o*-hydrazino-cinnamic acid and *o*-hydrazino-cinnamic lactam,  $C_6H_4 \begin{matrix} \swarrow [1]CH:CH:CO \\ \searrow [2]N(NH_2) \end{matrix}$ , m.p. 127° (*Fischer*, Ann. 221, 274).

(5) **CINNAMIC SULPHONIC ACIDS** are obtained by the action of fuming sulphuric acid on cinnamic acid (*Rudner*, Ann. 174, 8). The *m*-compound has been synthesised from *m*-benzaldehyde sulphonic acid (p. 280). *p*-Cinnamic sulphonic acid loses sulphonic acid groups in reduction and becomes hydrocinnamic acid (*Moore*, Am. 25, 622).

**HOMOLOGOUS CINNAMIC ACIDS** (*Auwers*, Ann. 413, 253). Cinnamic acids alkylated in the nucleus are obtained by the condensation of alkylated benzaldehydes with sodium acetate and acetic anhydride. The three tolylaldehydes give *o*-, *m*-, and *p*-methyl-cinnamic acids, m.p. 169°, 115° and 196°. With hydroxylamine these acids first form normal addition products,  $\beta$ -hydroxylamino-cinnamic acids, which then disproportionate giving  $\beta$ -amino- and  $\beta$ -isonitroso-derivatives of nucleus-methylated dihydro-cinnamic acids; finally either water or carbon dioxide is lost with the formation of isoxazolones, in the case of the former, and acetophenone oximes in the latter (*Posner*, Ber. 57, 1127). Cuminal gives *p*-cumenyl-acrylic acid,  $(CH_3)_2CH[4]C_6H_4CH:CHCOOH$ ; when this is nitrated it gives *p*- and *o*-nitrocumenyl-acrylic acids. The last-named acid shows reactions similar to those of *o*-nitro-cinnamic acid (*Widmann*, Ber. 19, 255).

**$\alpha$ -ALKYLATED CINNAMIC ACIDS** are obtained by the condensation of benzaldehyde with sodium propionate, butyrate, caproate, etc., and acetic anhydride (*Fittig*, Ann. 227, 57; *Michael*, Ber. 34, 918). Their *trans*-forms have been obtained by the oxidation of methyl-( $\alpha$ -alkyl)-styryl ketones with sodium hypochlorite. The styryl ketones are reaction products of benzaldehyde and alkyl-acetones (*Rinne*, Naturw. 18, 837).

**$\alpha$ -Methyl-cinnamic acid**,  $C_6H_5CH:C(CH_3)COOH$ , *cis*-form, m.p. 91°, two *trans*-forms, m.p. 82° and 74°, b.p. 288°, is also formed by the action of sodium on benzyl propionate (see p. 290), and by loss of water from  $\alpha$ -methyl- $\beta$ -phenyl-ethylene-lactic acid (p. 418) (*Edeleano*, Ber. 20, 617).  **$\beta$ -Phenyl-angelic acid**,  $\alpha$ -ethyl-cinnamic acid,  $C_6H_5\cdot CH:C(C_2H_5)COOH$ , m.p. 107° (*Claisen*, Ber. 23, 978).  **$\alpha$ ,*n*-Propyl-cinnamic acid**, m.p. 93°;  **$\alpha$ ,*n*-amyl-cinnamic acid** (*Rinne*, Naturw. 18, 837).  **$\alpha$ -Vinyl-cinnamic acid**, m.p. 92°, is obtained by the condensation of benzaldehyde and crotonic anhydride in the presence of trimethylamine, a migration of the double bond occurring (*Kuhn*, Ber. 64, 2347).

**$\beta$ -ALKYL-CINNAMIC ACIDS** are obtained by removal of water from  $\beta$ , $\beta$ -aryl-alkyl-hydracrylic acids, which are themselves the condensation products of aromatic ketones and bromoacetic ester, using zinc as condensing agent, or iodoacetic ester, using magnesium as condensing agent (*Schroeter*, Ber. 40, 1589; *Lindenbaum*, Ber. 50, 1270). When exposed to light, the  $\beta$ -alkyl-cinnamic acids are converted into the stereoisomeric allo-acids.

**$\beta$ -Methyl-cinnamic acid**,  $C_6H_5C(CH_3):CHCOOH$ , m.p. 98.5°, b.p. 167° (11 mm.), anilide, m.p. 121°, is obtained from dyphone oxime by means of the Beckmann transformation (*Henrich*, Ber. 37, 733).  **$\beta$ -Ethyl-,  $\beta$ -*n*-propyl-,  $\beta$ -isopropyl- and  $\beta$ -isobutyl-cinnamic acids**, m.p. 95.5°, 96.5°, 94°, and 85.5°.  **$\beta$ -Methyl-,  $\beta$ -ethyl-, and  $\beta$ -*n*-propyl-allocinnamic acids**, m.p. 131.5°, 93°, 86.5° (*Stoermer*, Ber. 50, 959).

**HIGHER PHENYL OLEFINE CARBOXYLIC ACIDS.** These are obtained from lactone-carboxylic acids by loss of carbon dioxide on heating, or from phenyl diolefine carboxylic acids on reduction.

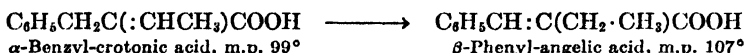
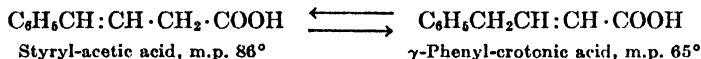
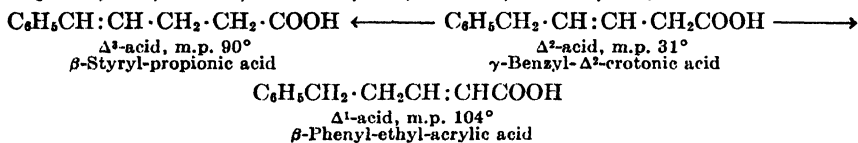
**Styryl-acetic acid,  $\beta$ -benzylidene-propionic acid, or "phenyl-isocrotonic acid,"**  $C_6H_5\cdot CH:CH\cdot CH_2\cdot COOH$ , m.p. 86°, b.p. 302° with partial decomposition into water and  $\alpha$ -naphthol, is obtained from phenyl-paraconic acid (p. 436) by loss of carbon dioxide and rearrangement (*Kipping*, J. 75, 144), from phenyl-cyclo-

propane-tricarboxylic acid,  $C_6H_5C(COOH) \begin{matrix} \swarrow CHCOOH \\ \searrow CHCOOH \end{matrix}$ , by heating (*Buchner*,

Ber. 25, 1155), and from phenyl-acetaldehyde and malonic acid by warming with pyridine. In the last reaction the phenyl-ethylidene-malonic acid first formed loses carbon dioxide and the double bond migrates (*Vorländer*, Ann. 345, 244). It combines with hydrobromic acid giving  $\gamma$ -phenyl- $\gamma$ -bromobutyric acid, and this

on treatment with sodium carbonate solution gives phenyl-butyrolactone. Styryl-acetic acid is also partly converted into butyrolactone by dilute sulphuric or hydrochloric acid, but with concentrated hydrochloric acid it condenses to a polymeric monohydric lactone acid, m.p. 179°. For syntheses carried out with styryl-acetic acid and mixed Grignard reagents, see *Ivanoff*, C.r. 197, 1230.  $\alpha$ - and  $\beta$ -Methyl-styryl acetic acids, m.p. 110° and 112° (*Fittig*, Ann. 255, 262).  $\gamma$ -Phenyl-crotonic acid,  $C_6H_5CH_2CH:CHCOOH$ , m.p. 65°, is obtained from  $\alpha$ -halogeno-phenyl-crotonic acids (*Bougaull*, C.r. 163, 481).  $\gamma$ -Benzyl- $\Delta^2$ -crotonic acid,  $C_6H_5CH_2CH:CHCH_2COOH$ , m.p. 31°, is obtained from  $\beta$ -styryl-acrylic acid (p. 480) by the action of sodium amalgam, or from  $\Delta^2$ - or  $\Delta^1$ -cinnamylidene-malonic acids on heating.  $\alpha$ -Benzyl-crotonic acid,  $C_6H_5CH_2C(:CHCH_3)COOH$ , m.p. 99°, is obtained from  $\alpha$ -benzyl- $\beta$ -hydroxybutyric acid.

The behaviour of these phenyl olefine carboxylic acids towards alkalis is noteworthy. While the aliphatic  $\beta,\gamma$ -unsaturated acids change, in the presence of alkali, to  $\alpha,\beta$ -unsaturated acids (Vol. I, p. 340), the aromatic olefine-carboxylic acids show at the same time a tendency for the double bond to migrate towards the phenyl group (*cf.* the change of  $\Delta^2$ - to  $\Delta^1$ -styrenes, p. 443). Thus, with caustic soda,  $\gamma$ -benzyl- $\Delta^2$ -crotonic acid gives a mixture of  $\Delta^1$ - and  $\Delta^2$ -acids (*Rieber*, Ber. 38, 2742);  $\gamma$ -phenyl-crotonic acid on simply warming with pyridine is almost completely converted into styryl-acetic acid (see above), a reaction which is partly reversed on boiling with caustic soda (*Fittig*, Ann. 283, 309).  $\alpha$ -Benzyl-crotonic acid gives phenyl-angelic acid when fused with caustic potash (*Fichter*, J. pr. 74, 334; *Thiele*, Ann. 319, 144; *Farmer*, J. 1933, 962).



$\beta$ -Styryl-propionic acid has been obtained by the distillation of  $\delta$ -phenyl- $\delta$ -valerolactone- $\gamma$ -carboxylic acid.

$\alpha$ -Halogeno-phenyl-crotonic acids,  $C_6H_5CH_2CH:C(Hlg)COOH$ , are obtained from  $\alpha,\alpha$ -dihalogeno-phenyl-butyric acids by warming the aqueous solutions of their sodium salts.

$\alpha$ -Bromophenyl-crotonic acid, m.p. stable form 96°, unstable form 100°.  $\alpha$ -Iodophenyl-crotonic acid, m.p. stable form 105°, unstable form 100° (*Bougaull*, C.r. 163, 481).

Atropic acid,  $\alpha$ -phenyl-acrylic acid,  $C_6H_5C \begin{smallmatrix} \nearrow COOH \\ \searrow CH_2 \end{smallmatrix}$ , m.p. 106–107°, is a struc-

tural isomer of cinnamic acid. It is obtained from tropic acid (p. 413), and from atrolactic acid (p. 413) by heating with hydrochloric acid or baryta. It is sparingly soluble in cold water, but dissolves readily in carbon disulphide, ether, and benzene. It is volatile with steam. It forms benzoic acid when oxidised with chromic acid, and gives  $\alpha$ -toluic and formic acids when fused with potash. It is converted into hydratropic acid by the action of sodium amalgam, and with hydrochloric acid and hydrobromic acid, it gives chloro- and bromo-hydratropic acids (p. 414). It combines with hydroxylamine forming  $\beta$ -hydroxylamino- $\alpha$ -phenyl-propionic acid (p. 295) (*Posner*, Ann. 389, 1). Like cinnamic acid it adds on sulphites to form salts of the sulphonic acid:  $C_6H_5CH(COOH)CH_2SO_3H$  (*Mulder*, Rec. 50, 719). When fused, or heated with water or hydrochloric acid for some time, it forms two dimeric isotropic acids, diatropic acids,  $(C_6H_5O_2)_2$ , m.p. 237° and 209°, which are related to atropic acid probably in the same way as the truxillic acids are to cinnamic acid (*Liebermann*, Ber. 28, 137). For the formulae of the isotropic acids, their interconversions, and their resolution into optical antipodes, see *Smith*, C. 1919, I, 835.

**$\beta$ -Chloro-atropic acid**,  $C_6H_5C(:CHCl)COOH$ , m.p. 119–120°, is obtained from hydroxymethylene-phenylacetic ester (p. 422) by the action of phosphorus pentachloride (*Wislicenus*, Ber. 51, 1366).

**$\alpha$ -Benzyl-acrylic acid**,  $C_6H_5CH_2C \begin{smallmatrix} \nearrow COOH \\ \searrow CH_2 \end{smallmatrix}$ , m.p. 68–69°, is obtained from benzyl-malonic ester and monochloro-methyl ether by the action of sodium, by boiling the benzyl-methoxy-methyl-malonic ester first formed with acetic acid and hydrochloric acid (*Simonsen*, J. 117, 564).

**Methyl-atropic acid**,  **$\alpha$ -phenyl-crotonic acid**,  $C_6H_5 \cdot C \begin{smallmatrix} \nearrow COOH \\ \searrow CH \cdot CH_3 \end{smallmatrix}$ , m.p. 135°, is obtained by the action of acetic anhydride on a mixture of phenylacetic acid and paraldehyde (*Oghaloro*, Gazz. 15, 514).

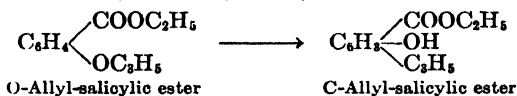
**$\alpha$ -Vinyl-phenylacetic acid**,  $C_6H_5CH(CH:CH_2)COOH$ , m.p. 23–24°, is formed by the action of carbon dioxide on cinnamyl-magnesium chloride, a migration of the double bond occurring (*Gilman*, Am. 53, 3541). **Allyl-phenylacetic acid**,  $C_6H_5CH(CH_2CH:CH_2)COOH$ , m.p. 34°, b.p. 260°, has been prepared from phenyl-allyl-malonic acid, and its nitrile has been obtained by the action of sodium hydroxide on a mixture of benzyl cyanide and allyl iodide (*Wislicenus*, Ber. 29, 2601).

### 11. Hydroxyphenyl Olefine Carboxylic Acids

In this group, as in that of the phenyl olefine carboxylic acids just dealt with, a distinction should be drawn between saturated hydroxyphenyl carboxylic acids, in which one atom of the benzene ring is replaced by an unsaturated group, and hydroxyphenyl fatty acids of which the side-chain contains a C:C linking.

#### I. HYDROXYPHENYL CARBOXYLIC ACIDS ALKYLENATED IN THE NUCLEUS

Just as the allyl group of the phenol-allyl ethers breaks its attachment to oxygen on heating, and migrates into the nucleus (p. 193), the allyl ethers of aromatic hydroxy-carboxylic acids and their esters undergo a similar change, giving hydroxy-acids with the allyl group in the nucleus (*Claisen*, Ber. 45, 3157; Ann. 401, 50):



Owing to the fact that they possess a free OH group, these esters dissolve in alkalis, give the ferric chloride reaction, and can be allylated a second time in the OH group. In the ring the allyl group occupies the free *o*-position relative to the phenolic oxygen; it is converted into propenyl by caustic potash, and into the propyl group by reduction. This reaction has been studied chiefly in connection with salicylic acid.

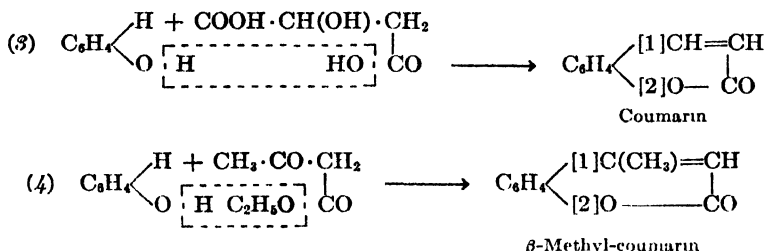
**C-Allyl-salicylic acid**, m.p. 96°; *ethyl ester*, b.p. 142° (12 mm.). **C-Propenyl-salicylic acid**, m.p. 158°. *Allyl-guaiacol-carboxylic acids* have been prepared by *Claisen* and have been used by him for the synthesis of *p*- and *o*-eugenol (Ann. 418, 69).

When citral (Vol. II, p. 204) is condensed with malonic ester and the product is treated with sodium ethylate, a phenol-carboxylic acid with an unsaturated group attached to the nucleus is obtained. It is 3-isoamenyl-4-methyl-salicylic acid,  $CH_3[4]C_6H_3CH_2CH_2[3]C_6H_3[2]OH[1]COOH$ , m.p. 167° (see p. 26).



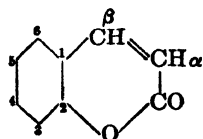
## II. HYDROXYPHENYL CARBOXYLIC ACIDS WITH A DOUBLE BOND IN THE SIDE-CHAIN

**A. MONOHYDROXY-PHENYL OLEFINE CARBOXYLIC ACIDS.** Formation: These acids are obtained (1) from the corresponding amino-phenyl olefine carboxylic acids by boiling their diazo-compounds in water (*Fischer*, Ber. 14, 479); or (2) by synthesis from phenol-aldehydes by heating them with a sodium salt and an anhydride of a fatty acid (Perkin's reaction). The internal anhydrides, or  $\delta$ -lactones of *o*-hydroxy-cinnamic acid, known as the coumarins, are obtained by the following syntheses devised by *Pechmann* (Ber. 34, 378, 421, 660): (3) the action of sulphuric acid on phenol and malic acid, when presumably the semi-aldehyde of malonic acid is the primary product, and then condenses with the phenol (*Simonis*, Ber. 48, 1583); and (4) the action of sulphuric acid or phosphorus pentoxide on phenols and acetoacetic or monoalkyl-acetoacetic esters. Phenol itself gives only a small yield of methyl-coumarin with acetoacetic ester, but polyhydric phenols, especially those containing two OH groups in the *m*-position, react more smoothly than the simple phenols (*Borsche*, Ber. 40, 2731):

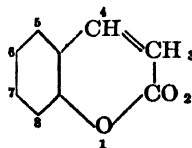


The first members of the series of hydroxyphenyl olefine monocarboxylic acids are the monohydroxy-cinnamic acids, which are obtained from the three amino-cinnamic acids by method (1). The *o*-hydroxy-cinnamic acids are particularly important. These, like cinnamic acid itself, exist in two stereoisomeric forms each. The *o*-coumaric acids correspond to the stable *trans*-form, and the *coumarinic acids* to the unstable *cis*-form. Free coumarinic acids are usually unstable, and by spontaneous loss of water form their  $\delta$ -lactones, known as *coumarins*. Salts, and mono- and di-alkyl ethers of coumarinic acids, are known, and are isomeric with the corresponding derivatives of the *o*-coumaric acids.

The members of the coumarin ring are numbered in two ways:



(old method)

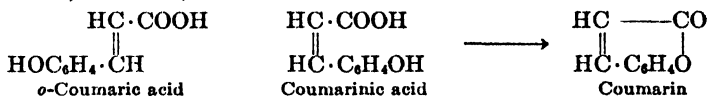


(new method)

In what follows, the old system will be used because of the relationship between coumarin and *o*-hydroxy-cinnamic acid. The new system is in general use for the flavylum compounds (Vol. II), derived from coumarin.

Sometimes the salts and ethers of coumarin are called  $\alpha$ -coumarates and those of *o*-coumaric acid,  $\beta$ -coumarates.

By substitution of the hydrogen atom which in coumarin occupies the *o*-position to the phenolic oxygen atom, a *nitro-coumarinic acid* is obtained, which can be liberated from its salts, and is distinguished from free 3-nitro-coumaric acid by the ease with which it loses water and forms 3-nitro-coumarin. The following steric formulae have therefore been suggested for *o*-coumaric and coumarinic acids, in order to explain the different tendencies of the acids to lose water (but see *Anschultz*, *Ann.* 254, 181).



Like cinnamic acid (p. 465) the stable *o*-coumaric acids and their derivatives are readily converted into the labile coumarinic acids by ultra-violet light, *i.e.*, by a suitable supply of energy. Thus *o*-coumaric acid gives coumarin directly (*Stoerner*, *Ber.* 44, 637). On boiling with dilute mineral acids, or under the influence of iodine in carbon disulphide, the *O*-alkyl-coumarinic acids change to the high-melting *O*-alkyl-coumaric acids (*Michael*, *Am. Ch. J.* 36, 552). An ortho-quinoid formula,  $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{COONa}$ , has been suggested by *Jordan* and *Thurpe* (*J.* 107, 387) for the yellow salts of unsubstituted coumarinic acids.

When *o*-coumaric acids in the solid state are exposed to light they dimerise and become *bis-coumaric acids*, which correspond to the truxillic acids (*Strom*, *Ber.* 37, 1383).

***o*-Hydroxy-cinnamic acid, *o*-coumaric acid**,  $\text{HO}[2]\text{C}_6\text{H}_4\text{CH}:\text{CH} \cdot \text{COOH}$ , m.p.  $208^\circ$ , is isomeric with hydrocoumarilic acid, phenylpyruvic acid, *etc.* It occurs together with *o*-hydrocoumaric acid in melilot, *Melilotus officinalis*, and in faham leaf from *Angraecum fragrans*. It is obtained from *o*-amino-cinnamic acid through the diazo-compound, and from coumarin by boiling with concentrated caustic potash, or better, sodium ethylate (*Miller*, *Ber.* 22, 1714). Its acetyl compound is obtained from sodio-salicylaldehyde and acetic anhydride (p. 472).

*o*-Coumaric acid dissolves readily in hot water and alcohol. It is not volatile with steam. It does not form coumarin when heated, although aceto-*o*-coumaric acid, obtained by the action of acetic anhydride or acetyl chloride, does. It is converted by sodium amalgam into *o*-hydrocoumaric or melilotic acid (p. 365) and alkalis decompose it into acetic and salicylic acids.

**2-Methoxy-cinnamic acid, methyl-*o*-coumaric acid**,  $\text{CH}_3\text{O}[2]\text{C}_6\text{H}_4[1]\text{CH}:\text{CH} \cdot \text{COOH}$ , m.p.  $185\text{--}186^\circ$ , is obtained from salicylaldehyde-methyl ether by the action of sodium acetate and acetic anhydride, and from methyl-coumarinic acid, m.p.  $93.6^\circ$  by rearrangement (p. 474). It is converted by sodium amalgam into methyl-ether-melilotic acid, and by bromine into methyl-ether-dibromomelilotic acid. With methyl alcohol, its amide, m.p.  $194\text{--}195^\circ$ , gives the *cis*- and *trans*-methyl esters of *o*-methoxy-styryl-carbamic acid (*Weerman*, *Rec.* 37, 1). **Methyl-2-methoxy-cinnamate**,  $\text{CH}_3\text{O}[2]\text{C}_6\text{H}_4[1]\text{CH}:\text{CH} \cdot \text{COOCH}_3$ , b.p.  $293^\circ$ , is obtained from the chloride by the action of methyl alcohol. **Aceto-*o*-coumaric acid**,  $\text{CH}_3\text{CO} \cdot \text{O}[2]\text{C}_6\text{H}_4\text{CH}:\text{CH} \cdot \text{COOH}$ , m.p.  $149^\circ$ , is obtained from salicylaldehyde, acetic anhydride and sodium acetate (see coumarin).

**3-Nitro-coumaric acid**,  $\text{NO}_2[3]\text{C}_6\text{H}_3[2](\text{OH})\text{CH}:\text{CH} \cdot \text{COOH}$ , is obtained by

digesting its dimethyl ether with caustic soda. Unlike 3-nitro-coumarinic acid, it is not decomposed by hot water, alcohol, or hydrogen bromide. Its *methyl-ether acid*, m.p. 193°, is obtained from 3-nitro-salicylaldehyde methyl-ether or from its *dimethyl-ether ester*, m.p. 88°, by the action of sodium carbonate (see above). The last-named compound is obtained from the silver salt of the methyl-ether acid by the action of methyl iodide (Miller, Ber. 22, 1710).

**Coumarin**, *benzo- $\alpha$ -pyrone*,  $C_6H_4 \begin{matrix} \swarrow [1]CH:CH \\ \searrow [2]O-CO \end{matrix}$ , m.p. 70°, b.p.

290°, is a constituent of glucosides found in woodruff, *Asperula odorata*, and in tonka beans from *Dipteryx odorata*, melilot, *Melilotus officinalis*, and in many other plants. In the laboratory it is obtained (1) by heating aceto-*o*-coumaric acid, the reaction product of acetic anhydride and sodio-salicylaldehyde, or of acetic anhydride and sodium acetate and salicylaldehyde (W. H. Perkin, Sr., Ber. 8, 1599; Ann. 147, 230); (2) from phenol and malic acid with sulphuric acid (p. 472); (3) from phenol and fumaric or maleic acid, with concentrated sulphuric acid or zinc chloride (Ger. Pat. 338,737); (4) from phenol or a phenol-sulphonic acid and maleic acid with dimethyl sulphate (Ger. Pats. 362,751/2); (5) from dihydrocoumarin (p. 365) by dehydrogenation with sulphur or chlorine (Ger. Pat. 276,667); (6) from coumarin-carboxylic acid (p. 488) by heating (Ger. Pat. 189,252); (7) from  $\beta$ -chloro- and  $\beta$ -bromo-coumarins (see below) by reduction. It has the fragrance of woodruff and is used in the tobacco industry and for the preparation of perfumes and essences.

Coumarin is fairly soluble in hot water, and freely in alcohol and ether. It dissolves in caustic potash with a yellow colour, a coumarinate being formed, from which solution coumarin is precipitated even by carbon dioxide. When boiled with concentrated caustic potash it is converted into a coumarate. It is reduced by sodium amalgam in aqueous solution to melilotic acid, and with sodium and alcohol to *o*-hydroxy-cinnamyl alcohol (Senmmler, Ber. 39, 2856; Auwers, Ann. 415, 98). With two molecules of a phenol in the presence of zinc chloride, it condenses to the so-called *coumareins*, the lactone ring being opened: **phenol-coumarein**,  $HO[2]C_6H_4CH:CH \cdot C(OH)(C_6H_4[4]OH)_2$ , m.p. 103–105° (Krishna, J. 119, 1420). With benzene and aluminium chloride, coumarin gives  $\beta$ -phenyl- $\alpha,\beta$ -dihydrocoumarin, m.p. 82° (King, Am. 49, 562). When coumarin vapours are passed through a tin-plate tube at 860°, coumarone (Vol. IV) is first formed (Orlow, Ber. 63, 2948). In sunlight it dimerises to hydro-dicoumarin.

$C_6H_4 \begin{matrix} \swarrow O-OC \\ \searrow CO-O \end{matrix} \begin{matrix} CH_2 \\ C=C \\ CH_2 \end{matrix} C_6H_4$ , m.p. 258°. When warmed in aqueous-alcoholic solution with potassium cyanide, hydrocyanic acid is added on, and hydrolysis of the compound gives *o*-hydroxyphenyl-succinic acid (p. 435) (Bredt, Ann. 293, 366). For the action of alkyl-magnesium halides and phenyl-magnesium halides, see Houben, Ber. 37, 389; Decker, Ann. 356, 295; 364, 1; for that of bisulphite, see Dodge, Am. 38, 446).

**Methyl ether of coumarinic acid**, m.p. 88°, and **methyl ether of methyl coumarinate**, b.p. 275°, obtained by heating sodium coumarinate and methyl iodide at 150°. Both are converted into the corresponding derivatives of *o*-coumaric acid by heating, and conversely are obtained from these by irradiation with ultra-violet light. **Coumaroxime**, m.p. 131° (Tiemann, Ber. 19, 1662), is obtained by the action of hydroxylamine on thiocoumarin.

**Coumarin bromide**,  $C_6H_3O_2Br_2$ , m.p. 105°, is obtained from coumarin by the action of bromine in carbon disulphide. With alcoholic potash it gives  $\alpha$ -bromo-

**coumarin**,  $C_6H_4 \begin{matrix} \swarrow [1]CH:CBr \\ \searrow [2]O-CO \end{matrix}$ , and both, on boiling with alcoholic potash, give

*coumarilic acid* (Vol. IV). For the action of iodine, or iodine and potassium iodide on coumarin, see *Simonis*, Ber. 50, 1139; *Dox*, Am. 39, 114. **Thion-**

**coumarin**,  $C_6H_4 \begin{matrix} \swarrow [1]CH:CH \\ [2]O-CS \end{matrix}$ , m.p. 101°, golden yellow needles, is obtained from

coumarin or *o*-coumaric acid by the action of phosphorus pentasulphide (*Tiemann*, Ber. 19, 1661). **Thiol-coumarin**,  $C_6H_4 \begin{matrix} \swarrow CH:CH \\ S-CO \end{matrix}$ , m.p. 80°, is obtained from *o*-mercapto-cinnamic acid by loss of water. It possesses a pleasant odour of cou-

marin (*Chmielewsky*, Ber. 46, 1906). **Dithio-coumarin**,  $C_6H_4 \begin{matrix} \swarrow CH:CH \\ S-CS \end{matrix}$ , wine-red crystals, m.p. 104°, is obtained by the action of phosphorus pentasulphide on thiol-coumarin (*Simonis*, Ber. 49, 763).

**3-Nitro-coumarinic acid**,  $NO_2 \cdot [3]C_6H_3 \begin{matrix} \swarrow [1]CH:CH \cdot COOH \\ [2]OH \end{matrix}$ , when rapidly heated melts and loses water at 150°, but when gently warmed in water or alcohol, it forms its anhydride, *3-nitro-coumarin*, from which it can be regenerated by boiling with sodium carbonate. It forms long yellow prisms. Its silver salt gives the methyl ether of 3-nitro-coumarinic acid methyl ester with methyl iodide.

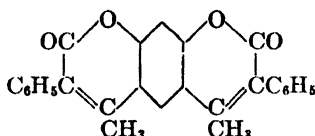
**HOMOLOGOUS COUMARINS.**  $\alpha$ -Alkyl-coumarins are obtained by method (2), p. 472, the anhydrides and sodium salts of propionic, butyric, and isovaleric acids being used as starting materials; or from  $\alpha$ -alkyl-malic acids by method (3).  $\beta$ -Alkyl-coumarins are prepared from phenols and acetoacetic ester with sulphuric acid (*Pechmann*, Ber. 17, 2188), by method (4).  $\alpha$ -Alkyl-thion-coumarins have been prepared from the  $\alpha$ -alkyl-coumarins and phosphorus pentasulphide, and  $\alpha$ -alkyl-cumaroximes have been prepared from them by the action of hydroxylamine (*Aldringen*, Ber. 24, 3459).  $\alpha$ -Methyl-coumarin,  $C_6H_4 \begin{matrix} \swarrow CH:C(CH_3) \\ O-CO \end{matrix}$ ,

m.p. 91°;  $\beta$ -methyl-coumarin,  $C_6H_4 \begin{matrix} \swarrow C(CH_3):CH \\ O-CO \end{matrix}$ , m.p. 82° (*Pechmann*, Ber.

34, 421); the former smells like coumarin, and is destroyed by permanganate, while the latter is odourless and is hardly affected by permanganate (*Angeli*, Gazz. 61, 276).

For other homologous coumarins, see *Fries*, Ber. 39, 871; Ann. 362, 1; 379, 90; *Churt*, Bull. 35, 76; *Peters*, Ber. 41, 830; *Anschütz*, Ann. 367, 232; *Clayton*, J. 93, 2016; *Posner*, Ber. 46, 3816; *Bailey*, Ind. Eng. 13, 905; *Wittig*, Ber. 57, 88; *Müller*, Ber. 58, 2202; *Canter*, J. 1931, 1255; *Robertson*, J. 1931, 2426; (Ger. Pat. 338,737).

For *dicoumarins* such as



which are obtained from diaceto-resorcinol and sodium phenyl-acetate, see C. 1932, II, 1430.

*p*-Amino- $\beta$ -methyl-coumarin, mono- and dimethyl-amino- $\beta$ -methyl-coumarin, m.p. 230°, 123° and 143°, are obtained from amino-, methyl-amino-, and dimethyl-amino-phenol and acetoacetic ester (*Pechmann*, Ber. 30, 277; 32, 3690).

*m*-Coumaric acid,  $HO[3]C_6H_4 \cdot CH:CH \cdot COOH$ , m.p. 191°, occurs in xanthorrhoea resins, etc. It has been prepared from *m*-amino-cinnamic acid and from *m*-hydroxy-benzaldehyde (*Tiemann*, Ber. 15, 2049; *Gabriel*, *ibid.*, 2297). For nitro-*m*-coumaric acids, see *Luff*, Ber. 22, 292. *o*-Amino-*m*-coumaric acid has been obtained by the electrolysis of *o*-nitro-cinnamic acid (*Gattermann*, Ber. 27, 1936).

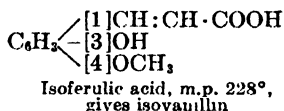
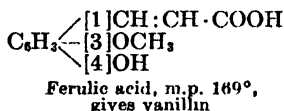
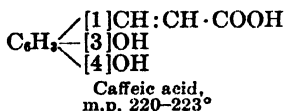
**p-Coumaric acid**,  $\text{HO}[4]\text{C}_6\text{H}_4\text{CH}:\text{CH}\cdot\text{COOH}$ , m.p.  $206^\circ$ , is obtained (1) from *p*-amino-cinnamic acid; (2) from *p*-hydroxy-benzaldehyde (Konek, Ber. 51, 856); (3) by boiling extract of aloes with sulphuric acid (Eigel, Ber. 20, 2528); and (4) by the decomposition of the glucoside *naringin* (Vol. IV). *trans*-Methyl-*p*-coumaric acid occurs in the oil of *Andropogon odoratus*, and has been synthesised from anisaldehyde. It forms liquid crystals and consequently possesses two melting points: liquid-crystalline, m.p.  $171^\circ$ , and isotropic, m.p.  $186^\circ$  (Stoermer, Ber. 44, 639). The *cis*-acid melts at  $65^\circ$ .  $\alpha$ -Benzoyl-amino-*p*-coumaric acid, see p. 416. The *p*-methoxyphenyl and *p*-ethoxyphenyl esters of *p*-methoxy-cinnamic acid also form liquid crystals (Vorländer, Z. Kryst. 79, 61).

When phenol-alkyl ethers of coumaric acids are treated first with hydrobromic acid and then with aqueous sodium carbonate, they lose carbon dioxide and form ethers of unsaturated phenols, cf. *o*- and *p*-vinyl-anisole, p. 449. This reaction recalls the formation of styrene from  $\beta$ -bromo-hydrocinnamic acid (p. 443).  $\beta$ ,*p*-Methoxyphenyl-methacrylic acid,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_3\text{CH}:\text{C}(\text{CH}_3)\text{COOH}$ , m.p.  $154^\circ$ , is obtained from anisaldehyde and propionic acid; when heated it decomposes into carbon dioxide and anethole (p. 450).

## B. DIHYDROXY-PHENYL OLEFINE CARBOXYLIC ACIDS.

Among the known dihydroxy-cinnamic acids the most important are: *caffeic acid*, 3,4-dihydroxy-cinnamic acid, which corresponds to protocatechuic acid (p. 365), and *umbellic acid*, 2,4-dihydroxy-cinnamic acid. Both these compounds, and their simple derivatives are found in plants, or are among the decomposition products of vegetable substances. Also, 3-methyl-caffeic or ferulic acid can be converted into vanillin (p. 347).

**Caffeic acid**,  $\beta$ -3,4-dihydroxy-phenyl-acrylic acid, 3,4-dihydroxy-cinnamic acid, and its methyl and methylene ether acids are reduced to hydrocaffeic acid and its ether acids (p. 369), and oxidised to protocatechuic acid and its ethers. When the aceto-derivatives of the two methyl-ether caffeic acids are oxidised with permanganate, the first products are the aceto-compounds of the two methyl ether protocatechu-aldehydes. Conversely caffeic acid and its ether acids have been synthesised by Perkin's and Knoevenagel's reactions (p. 463). Caffeic acid and its ether acids give protocatechuic and acetic acids when fused with potash.



Caffeic acid is formed when chlorogenic acid (Vol. II, p. 136) is boiled with caustic potash. It occurs in cowbane, *Cicuta virosa* (Hofmann, Ber. 17, 1922), and in the leaves of *Anthemis nobilis*, the true camomile (Power, J. 105, 1829). Its solution gives a green colour with ferric chloride, which turns dark red on addition of sodium carbonate. A very delicate reaction is the vermilion colour obtained when an acidified solution of caffeic acid is added to an aqueous solution of an alkali nitrite (Hoepfner, Ch. Ztg. 56, 991).

**Ferulic acid**, *m*-methoxy-*p*-hydroxy-cinnamic acid, occurs in Asafoetida resin and has been obtained from vanillin (Arch. Pharm. 269, 331), and from *m*-methoxy-*p*-nitro-cinnamic acid, which is obtained by the action of nitric acid on ethyl-*m*-methoxy-cinnamate (Ger. Pat. 32,914). Acetyl compound, m.p.  $196^\circ$ .

**Isoferulic acid**, *m*-hydroxy-*p*-methoxy-cinnamic acid, *hesperitinic acid*, was first obtained as a decomposition product of the glucoside *hesperitin* (Vol. IV). It has been prepared by Robinson (J. 1931, 3163) from isovanillin and malonic acid in the presence of pyridine, and by Mauthner (J. pr. 104, 132) from *m*-nitro-*p*-methoxy-cinnamic acid. By partial methylation of caffeic acid, both these ethers are obtained, isoferulic acid being the chief product. Acetyl compound, m.p.  $199^\circ$ . **Dimethyl-caffeic acid**,  $(\text{CH}_3\text{O})_2[3,4]\text{C}_6\text{H}_2\text{CH}:\text{CH}\cdot\text{COOH}$ , m.p.  $181^\circ$  (Tiemann, Ber. 14, 959; Perkin, J. 85, 159). **Piperonyl-acrylic acid**,  $(\text{CH}_2\text{O}_2)-[3,4]\text{C}_6\text{H}_3\text{CH}:\text{CH}\cdot\text{COOH}$ , m.p.  $242^\circ$  (Feuerstein, Ber. 34, 1469). Its *isobutyl*-

amide, *fagaramide*, m.p. 119–120° (Vol. II, p. 406) is found in the oil from the root of a rutacea, *Fagara xanthoxyloides*. **Diaceto-caffeic acid**,  $(\text{CH}_3\text{CO}_2)_2[3,4]\text{-C}_6\text{H}_2\text{CH:CH}\cdot\text{COOH}$ , m.p. 190° (*Tiemann*, Ber. 11, 656).

For caffeic acid derivatives containing two different acyl groups and for the migration of acyl groups which takes place on their partial hydrolysis, see *Pacsu*, Ber. 59, 2818; 62, 2974, and p. 370.

**$\alpha$ -Homocaffeic acid**, 3,4-dihydroxy- $\alpha$ -methyl-cinnamic acid, m.p. 193°. Its monomethyl ether acid, *homoferulic acid*,  $(\text{CH}_3\text{O})(\text{OH})[3,4]\text{C}_6\text{H}_2\text{CH:C}(\text{CH}_3)\text{-COOH}$ , m.p. 168°, gives isoeugenol (p. 453) when heated with lime (*Tiemann*, Ber. 15, 2063).

**$\alpha$ -Hydropiperic acid**,  $(\text{CH}_2\text{O}_2)[3,4]\text{C}_6\text{H}_2\text{CH}_2\cdot\text{CH:CH}\cdot\text{CH}_2\text{COOH}$ , m.p. 78°, is obtained from piperic acid (p. 481) by the action of sodium amalgam. On boiling with caustic soda it rearranges to  **$\beta$ -hydropiperic acid**,  $(\text{CH}_2\text{O}_2)[3,4]\text{C}_6\text{H}_2\cdot\text{CH}_2\cdot\text{CH:CH}\cdot\text{COOH}$ , m.p. 131°. When this is acted upon by sodium amalgam it gives the so-called *piper-hydronic acid*,  $(\text{CH}_2\text{O}_2)[3,4]\text{C}_6\text{H}[\text{CH}_2]_4\text{COOH}$ , m.p. 98° (p. 369).

**Umbellic acid**, 2,4-dihydroxy-cinnamic acid,  $(\text{HO})_2[2,4]\text{C}_6\text{H}_2\cdot\text{CH:CH}\cdot\text{COOH}$ , decomp. about 240°, is obtained from umbelliferone by boiling with caustic potash. **2,4-Dimethoxy-cinnamic acid**, m.p. 184°, has been synthesised from dimethyl-resorcyaldehyde by Perkin's reaction (*Perkin*, J. 85, 159).

**Umbelliferone**, 4-hydroxy-coumarin,  $\text{HO}[4]\text{C}_6\text{H}_2\begin{matrix} \text{[1]CH:CH} \\ \text{[2]O—CO} \end{matrix}$ , m.p. 240°, fluoresces in solution (*Meyer*, Ber. 31, 513; *Kunz*, *ibid.*, 1189). It is found in the bark of *Daphne mezereum*, and among the distillation products of various umbellifera resins, such as *Galbanum* and *Asafoetida*. It has been synthesised from  $\beta$ -resorcyaldehyde by method (2), and from resorcinol and malic acid, or fumaric or maleic acid, by method (3) (*George*, Soc. South Agr. 13, 255). It smells like coumarin, and behaves in a similar way towards caustic potash, with which it gives a blue fluorescence (*Day*, J. Indian Chem. Soc. 8, 817). The isomerism of its alkyl ethers is similar to that of *o*-coumaric acid and coumarin (p. 474) (*Will*, Ber. 19, 1778); its methyl ether, *herniarin*, m.p. 117–118°, occurs in oil of lavender, in *Herniaria hirsuta*, etc. (*Power*, J. 105, 2285).

**$\beta$ -Methyl-umbelliferone**, 4-hydroxy- $\beta$ -methyl-coumarin, *resocyanin*,  $\text{HO}[4]\text{-C}_6\text{H}_2\begin{matrix} \text{[1]C}(\text{CH}_3)\text{:CH} \\ \text{[2]O—CO} \end{matrix}$ , m.p. 185°, is obtained from resorcinol and acetoacetic ester, or aceto-cyano-acetic ester with sulphuric acid, and also from *p*-amino-methyl-coumarin (p. 475) (*Held*, C.r. 116, 720). When fused with caustic potash it gives resacetophenone (p. 352). Its ethyl ether, m.p. 115°, which is prepared in a similar manner from resorcinol-monoethyl ether has a taste of maple sugar (U. S. Pat. 1,934,361). Umbelliferone and methyl-umbelliferone have been used as fluorescent indicators in volumetric analysis (*Robl*, Ber. 59, 1725; *Malowan*, Ch. Ztg. 57, 755). For **nitro-** and **amino-methyl-umbelliferones**, see *Pechmann*, Ber. 34, 660.  **$\alpha,\beta$ -Dimethyl-umbelliferone**, m.p. 256°, (*id.*, Ber. 16, 2127). Analogous compounds are obtained from orcinol by methods (3) and (4) (p. 472) (*id.*, Ber. 17, 1649, 2188).

Two coumarin derivatives with unsaturated alkyl side-chains occur in *Imperatoria ostruthium*. They are **osthole**, 3- $\Delta^2$ -isoameryl-4-methoxy-coumarin, and **osthrutin**, 5-isononadienyl-4-hydroxy-coumarin. These and their degradation products are dealt with in Vol. II, p. 499.

**2,5-Dihydroxy-cinnamic acid**, m.p. 207°, is obtained from *o*-coumaric acid by the action of permanganate in alkaline solution (*Neubauer*, Physiol. 52, 375).

**3,5-Dihydroxy-cinnamic acid**, m.p. 244–245° (with  $\frac{1}{2}\text{H}_2\text{O}$ ), has been prepared by Perkin's method from diacetyl- $\alpha$ -resorcyaldehyde (*Asahina*, Pharm. Japan, 1924). **5-Methoxy-3-hydroxy-cinnamic acid**, m.p. 198–199°, is obtained from the corresponding aldehyde, m.p. 130°, by the action of malonic acid and piperidine (*Mauthner*, J. pr. 116, 314).

**3-Hydroxy-coumarin**, m.p. 280–285°, and **5-hydroxy-coumarin**, m.p. 249°, are obtained from pyrocatechol and hydroquinone by the action of malic acid and sulphuric acid (*Bizzari*, Gazz. 15, 33); the 5-derivative is also formed when coumarin is oxidised by potassium persulphate in the presence of ferrous sulphate (*Bargellini*, Gazz. 45, I, 90). **3-Methoxy-coumarin**, m.p. 89°, has been obtained

from *o*-vanillin by Perkin's reaction (Arch. Pharm. 253, 33). **5-Hydroxy- $\beta$ -methyl-coumarin**, m.p. 243°, is obtained from hydroquinone, acetoacetic ester and sulphuric acid (*Borsche*, Ber. 40, 2731).

**C. TRIHYDROXY-CINNAMIC ACIDS.** Two  $\delta$ -lactones of trihydroxy-cinnamic acids, **daphnetin**, 3,4-dihydroxy-coumarin, m.p. 255°, and **aesculetin**, 4,5-dihydroxy-coumarin, m.p. 268–270°, are the aromatic constituents of the isomeric glucosides *daphnin*, *aesculin* (Vol. II, p. 358), and *cichorin* (Arch. Pharm. 270, 476). The one has been synthesised from pyrogallaldehyde and the other from hydroxy-hydroquinone-aldehyde (p. 350) by the action of acetic anhydride and sodium acetate (*Gallermann*, Ber. 32, 287). The corresponding trihydroxy-cinnamic acids, **aesculetinic** and **daphnetinic acids**, are known in the form of their ether acids or ether esters. The triethyl ethers are oxidised by permanganate to triethoxy-benzoic acids, which lose carbon dioxide and are converted into triethoxy-benzenes (*Tiemann*, Ber. 15, 2082; *Will*, Ber. 17, 1086; 20, 1119).

**Dimethyl-daphnetin**, 3,4-dimethoxy-coumarin, m.p. 119–121°, has been obtained by methylating daphnetin (*Bargellini*, Gazz. 46, I, 249).

**Methyl-aesculetin**, 4-hydroxy-5-methoxy-coumarin, *scopoletin*, m.p. 204°, occurs both in the free state and as glucoside in *Solanaceae* and *Scopolia* species, and is identical with *gelseminic acid* from *Gelsemium sempervirens* and with *chrysotropic acid* from *Atropa belladonna* (*Kunz-Krause*, Ber. 31, 1189). It shows a strong fluorescence. **5-Hydroxy-4-methoxy-coumarin**, m.p. 185–186°, is obtained from umbelliferone-methyl ether by the action of potassium persulphate (*Bargellini*, Gazz. 45, I, 90) and from aesculetin by the action of methyl iodide or diazomethane. **Dimethyl-aesculetin**, m.p. 142–143° (Arch. Pharm. 270, 479).  **$\beta$ -Methyl-aesculetin**, 4,5-dihydroxy- $\beta$ -methyl-coumarin, m.p. 272–274°, is obtained from hydroxy-hydroquinone triacetate by the action of acetoacetic ester and sulphuric acid (*Pechmann*, Ber. 34, 423; *Vliet*, Org. Synth. 1, 352).

**Sinapic acid**, hydroxy-dimethoxy-cinnamic acid,  $(\text{CH}_3\text{O})_2[3,5](\text{OH})[4]-\text{C}_6\text{H}_2\text{CH}:\text{CHCOOH}$ , m.p. 192°, has been obtained from white and black mustard seed (Vol. II, p. 368), and synthetically from syringaldehyde by Perkin's reaction (*Graebe*, Ber. 36, 1031; *Späth*, Mo. 41, 271). **Methyl-sinapic acid**, 3,4,5-trimethoxy-cinnamic acid, m.p. 126.8°, is obtained from trimethyl-gallaldehyde (*Mauthner*, Ber. 41, 2531). **2,3,4-Trimethoxy-cinnamic acid**, m.p. 172°, is obtained from the corresponding derivative of benzaldehyde (*Slotta*, Ber. 63, 3029). **2,4,5-Trimethoxy-cinnamic acid**, *trimethyl-aesculetinic acid*, m.p. 169°, has been obtained from asarylaldehyde (p. 350) by Perkin's synthesis.

**4,6-Dihydroxy-coumarin**, m.p. 273°, is obtained from phloroglucin-aldehyde by Perkin's reaction, and on methylation gives **citropten**, *limetin*, 4,6-dimethoxy-coumarin, m.p. 147°, which separates from the essential oils of some species of citrus (*Tilden*, J. 81, 508; *Schmidt*, Arch. Pharm. 242, 288).

**4,6-Dihydroxy- $\alpha$ -methoxy-coumarin**, m.p. 280–285° (decomp.), is obtained from phloroglucinol diacetate with methoxy acetic anhydride and the sodium salt. **4,6- $\alpha$ -Trimethoxy-coumarin**, m.p. 171–172°, is related to *pelargonidin*, the colouring matter of some flowers (see Vol. II, p. 449; Vol. IV) (*Willstätter*, C. 1914, II, 1360). For other di- and tri-hydroxycoumarins, see *Sonn*, Ber. 50, 1292; *Chakravarti*, Ber. 64, 354; *Canter*, J. 1931, 1255.

**D. TETRAHYDROXY-CINNAMIC ACIDS.** **Fraxetin**, m.p. 227°, is the aromatic component of the glucoside *fraxin* (Vol. II, p. 358). It is the 5-methyl ether of 3,4,5-trihydroxy-coumarin, m.p. 272°. It has been synthesised from 1,2,3,4-tetrahydroxybenzene (p. 232) through tetrahydroxy-benzaldehyde and triaceto-hydroxycoumarin, m.p. 144.5°. Trimethyl ether, m.p. 102–104° (*Wessely*, Mo. 60, 163).

## 12. Phenyl-acetylene Carboxylic Acids

**Phenyl-propionic acid**,  $\text{C}_6\text{H}_5\cdot\text{C}:\text{C}\cdot\text{COOH}$ , m.p. 136°, is obtained from  $\alpha$ - and  $\beta$ -bromocinnamic acids by boiling with alcoholic potash, from sodio-phenylacetylene (p. 447) by the action of carbon dioxide (*Glaser*, 1870), and from  $\omega$ -bromostyrene (p. 444) by the action of carbon dioxide and sodium. It is prepared by boiling the dibromide of cinnamic acid or ester with alcoholic potash (*Michael*, Ber. 34, 3647; 36, 902; *Abbott*, Org. Synth. 12, 60). It decomposes into phenyl-

acetylene and carbon dioxide when heated with water to 120°. When warmed with acetic anhydride or treated with phosphorus oxychloride, phenyl-propionic acid forms 1-phenyl-naphthalene-2,3-dicarboxylic anhydride (*Bucher*, *Am.* 30, 1244; *Pfeiffer*, below). Similarly phenyl-propionic ester polymerises to phenyl-naphthalene-dicarboxylic ester at 200° (*Pfeiffer*, *Ber.* 40, 3372, 3839). See p. 395 on the formation of trimesic acid from propiolic acid.

When phenyl-propionic acid adds on hydrogen under the action of sodium amalgam, hydrocinnamic acid is formed, but with zinc dust and acetic acid, or sodium and alcohol, cinnamic acid is produced (*Aronstein*, *Ber.* 22, 1181), and with hydrogen in the presence of colloidal palladium, allocinnamic acid is formed (*Paal*, *Ber.* 42, 3930). Hydrochloric and hydrobromic acids add on with the formation of  $\beta$ -halogeno- and allo- $\beta$ -halogeno-cinnamic acids (p. 466). It combines with the halogens to form phenyl-dihalogeno-acrylic acids (p. 467), with hydrazine hydrate to give 1-phenyl-3-pyrazolone (Vol. IV), and with phenyl-hydrazine to give 1,3-diphenyl-pyrazolone (*Rothenburg*, *Ber.* 27, 783). It enters into similar reactions with other amino-bases, and with the sodio-compounds of  $\beta$ -diketones, acetoacetic and malonic esters (*Ruhemann*, *Proc.* 1900, 11; *Moureu*, *Bull.* 1, 1071). In the latter reaction a tricarboxylic acid is formed which gives phenyl-glutaconic acid with loss of carbon dioxide (*Michael*, *J.* pr. 49, 20; *Carrington*, *J.* 75, 778). Phenyl-propionic acid adds on one or two molecules of alcohol when heated with a sodium alcoholate, and  $\beta$ -alkoxy-cinnamic esters (p. 484) or dialkyl-acetals of benzoyl-acetic esters are formed (*Moureu*, *C.r.* 138, 206; 142, 894). It condenses with phenethynyl-magnesium bromide to give *tris-phenethynyl-carbinol*,  $(C_6H_5C:C)_3C \cdot OH$ , m.p. 126–128° (*Hess*, *Ber.* 54, 2511). Phenyl-propionic nitrile combines with one molecule of a primary or secondary amine to form  $\beta$ -alkylamino-cinnamic nitriles, such as  $C_6H_5C(NHCH_3):CH \cdot CN$ ; these regenerate the amines when acted upon by acids, and are converted into benzoyl-acetonitrile (*Moureu*, *C.r.* 143, 553).

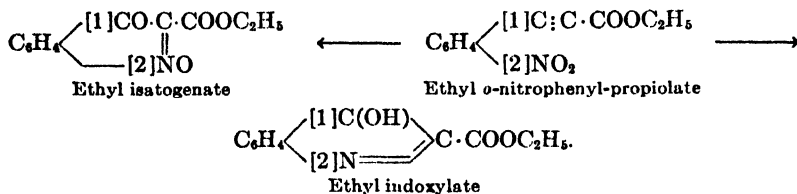
Ethyl phenyl-propionate,  $C_6H_5C:C \cdot COOC_2H_5$ , b.p. 153° (22 mm.), can be obtained from sodio-phenylacetylene by the action of chlorocarbonic ester, and it readily adds on water to form benzoyl-acetic ester (p. 429). With nitrogen peroxide at 0°, it forms  $\alpha, \beta$ -dinitro-cinnamic ester, which exists as an oil, and as a solid, m.p. 60°; the former modification is thought to be the *cis*-form and the latter the *trans*-form (*Wieland*, *Ber.* 53, 1343). For addition products with phenols, thiophenols, naphthols, and thionaphthols, see *Ruhemann*, *Ber.* 47, 119. Phenylpropionic nitrile,  $C_6H_5C:CCN$ , m.p. 41°, is obtained from the amide by the action of phosphorus pentoxide, from sodio-phenylacetylene or phenylacetylene magnesium bromide by the action of cyanogen or cyanogen chloride (*Grignard*, *Bull.* 17, 228), and from phenyl-propargyl-aldoxime by the action of acetic anhydride (*Claisen*, *Ber.* 36, 3671). Chloride, b.p. 131° (25 mm.); amide, m.p. 102° (*Baucke*, *Rec.* 15, 123; *Moureu*, *C.r.* 142, 211; *Stockhausen*, *Ber.* 25, 3537). The hydrazide melts at 114°, and re-solidifies with the formation of 3-phenyl-5-pyrazolone, m.p. 235° (Vol. IV) (*Curtius*, *J.* pr. 112, 314).

**o-Nitrophenyl-propionic acid**, decomposes at 156°. It is prepared from *o*-nitrocinnamic ester dibromide by boiling with alcoholic potash (*Baeyer*, *Ann.* 212, 140). Its silver salt explodes when heated. When boiled with water it loses carbon dioxide, and gives *o*-nitrophenyl-acetylene, and when boiled with alkalis it is converted into isatin. In concentrated sulphuric acid it dissolves with isomerisation to isatogenic acid, which at once decomposes into carbon dioxide and isatin. When heated with alkaline reducing agents, such as glucose and caustic potash, potassium xanthogenate, or hydrogen sulphide and ferrous sulphate, it is smoothly converted into *indigo blue* (*Baeyer*, 1880).

Ethyl *o*-nitrophenyl-propionate, m.p. 60°, is prepared from the acid by the action of alcohol and hydrochloric acid. When dissolved in sulphuric acid it

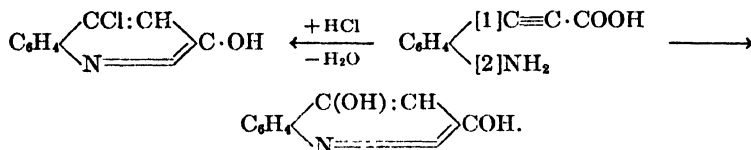


changes into ethyl isatogenate, and with ammonium sulphide gives ethyl indoxylate (*Baeyer*, Ber. 14, 1741):



**p-Nitrophenyl-propionic acid**, m.p. 198° (decomp.), is obtained from the dibromide of *p*-nitrocinnamic ester, and by the nitration of phenyl-propionic acid at -20°. When boiled with water it breaks down into carbon dioxide and *p*-nitrophenyl-acetylene (p. 447). When heated with sulphuric acid to 100°, it is converted into *p*-nitro-acetophenone (p. 286). Its ethyl ester, m.p. 126°, gives *p*-nitrobenzoyl-acetic acid when treated with sulphuric acid at 35°. **m-Azoxyphenyl-propionic acid**, m.p. 208°, is obtained from *m*-nitrophenyl- $\alpha$ , $\beta$ -dibromopropionic acid by the action of alcoholic potash (*Reich*, C.r. 162, 129; Bull. 19, 146).

**o-Aminophenyl-propionic acid**, m.p. 129° (decomp. into CO<sub>2</sub> and *o*-amino-phenyl-acetylene, p. 447), is obtained by reduction of *o*-nitrophenyl-propionic acid with ferrous sulphate and ammonia (*Richter*, Ber. 16, 679). It separates as a yellow crystalline powder. It forms *o*-amino-acetophenone when boiled with water,  $\gamma$ -chloro-carbostyryl when boiled with hydrochloric acid, and  $\gamma$ -hydroxy-carbostyryl when warmed with sulphuric acid (*Baeyer*, Ber. 15, 2147).



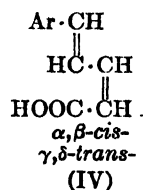
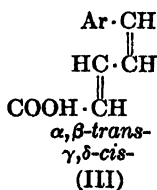
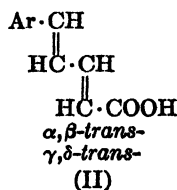
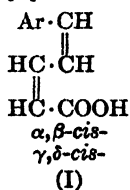
Its diazo-chloride, obtained by the action of sodium nitrite on its hydrochloride, gives hydroxycinnoline-carboxylic acid when warmed to 70° (Vol. IV).

**m-Methylphenyl-propionic acid**, CH<sub>3</sub>[3]C<sub>6</sub>H<sub>4</sub>·C:C·COOH, m.p. 109° (*Muller*, Ber. 20, 1215).

Nitriles of higher phenylacetylene-carboxylic acids have been prepared by *Grignard* (Ann. chim. [10], 5, 5) from phenylacetylene magnesium halides and cyanogen chloride.

### 13. Phenyl Diolefine Carboxylic Acids

The most interesting compounds in this group are the  $\delta$ -phenyl-butadiene-carboxylic acids, Ar·CH:CH·CH:CHCOOH. Of the four configurations theoretically possible:



three are known.

**Cinnamal-acetic acid**,  $\beta$ -styryl-acrylic acid (form II), m.p. 165°, is obtained together with form (III), **allocinnamal-acetic acid**, m.p. 138°, from cinnamic aldehyde and malonic acid in the presence of pyridine; cinnamal-malonic acid is an intermediate product (*Doebner*, Ber. 35, 2137). It has also been obtained from cinnamal-pyruvic acid (p. 486) by the action of hydrogen peroxide (*Friedmann*,

Helv. 14, 1213), and from cinnamic aldehyde, acetic anhydride and sodium acetate heated in a sealed tube at 160° (J. 31, 403). The allo-acid has been prepared by *Doebner* (Ber. 36, 4322) from cinnamic aldehyde and malonic acid in the presence of quinoline at 130°. When warmed in benzene with a little iodine and in sunlight, the allo-acid changes to the higher melting form (*Liebermann*, Ber. 28, 1443; *Stobbe*, Ber. 45, 3408). A third isomer, which corresponds to (IV), m.p. 128°, has been obtained by the action of zinc and alcohol on  $\gamma$ -bromocinnamal-acetic acid, the latter being obtained from  $\alpha$ -bromo-cinnamic aldehyde. Here, the acid of m.p. 165° is a by-product (*Lohaus*, Ann. 513, 228). The  $\gamma,\delta$ -cis-configuration is unstable in the presence of alcoholic potash, and to some extent changes to the  $\gamma,\delta$ -trans-form. The acid of m.p. 165°, when rapidly heated, loses carbon dioxide, and is converted into phenyl-butadiene (p. 448) (*Liebermann*, Ber. 35, 2696). Its chloride gives a piperidine, m.p. 92°, which has a hot taste, two or three times more intense than that of natural piperine (see below). The acrid taste of these piperidides is related to the two double bonds of the acid (*Staudinger*, Ber. 56, 699, 711). For the methyl esters of these acids, see *Stobbe*, Ber. 45, 3396, and for their ethyl esters, see *Auwers*, J. pr. 105, 377. Cinnamal-cyanoacetic acid (p. 489) gives a nitrile, b.p. 285°. Cinnamal-acetic acid as well as the allo-acid dimerise in the light, giving an acid of m.p. 219°. The  $\alpha,\beta$ -double bond of one molecule seems to combine with the  $\gamma,\delta$ -double bond of a second to form a cyclobutane ring (*Rieber*, Ber. 46, 335). *o*- and *p*-Nitro-acids, m.p. 217° and 271°, have been obtained from *o*- and *p*-nitrocinnamylidene-acetones by the action of sodium hypochlorite (*Einhorn*, Ann. 253, 356). *o*-Amino-acid, m.p. 176° (decomp.) (*Diehl*, Ber. 18, 2332).

**$\beta$ -Styryl-crotonic acid**,  $\text{C}_6\text{H}_5\text{CH}:\text{CH} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{H}_3\text{C} \quad \text{COOH} \\ \quad \quad \text{H} \end{array}$ , m.p. 124°, is obtained

through its ethyl ester from benzylidene-acetone and bromoacetic ester and zinc. When its benzene solution is exposed to light in the presence of a little iodine, its

geometrical isomer,  $\text{C}_6\text{H}_5\text{CH}:\text{CH} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{CH}_3 \quad \text{H} \\ \quad \quad \text{COOH} \end{array}$ , m.p. 160°, is formed (*Kuhn*,

Ber. 65, 651).

**$\gamma$ -Styryl- $\Delta^2$ -crotonic acid**,  $\text{C}_6\text{H}_5\text{CH}:\text{CH} \cdot \text{CH}:\text{CH} \cdot \text{CH}_2\text{COOH}$ , m.p. 112, is obtained in small yield when cinnamaldehyde and sodium succinate condense under the influence of acetic anhydride (*Fittig*, Ann. 331, 162).  **$\alpha$ -Cinnamal-propionic acid**, see *Baidakovsky*, Russ. 37, 896.

**Dihydroxy-phenyl-butadiene-carboxylic acids**. These can also exist in four forms, like their parent acids. Three of them are known. *Piperic acid* (form II), where  $\text{Ar} = \text{CH}_2\text{O}_2[3,4]\text{C}_6\text{H}_3$ , m.p. 217°, is obtained together with piperidine (Vol. IV) by the hydrolysis of piperine with alcoholic potash. *Isopiperic acid* (form IV?) is obtained from "piperonylidene malonic acid" (p. 489) by loss of carbon dioxide. *Chavicin*, obtained from black pepper, gives *chavicinic acid* (form I) on hydrolysis with alcoholic potash. This acid is unstable, and rearranges to *isochavicinic acid* (form III?), m.p. 200–202° (*Ott*, Ber. 55, 2633; cf. *Lohaus*, Ann. 513, 228). When fused with potash, piperic acid gives acetic, oxalic, and protocatechuic acids (p. 365). Its chloride is converted into piperine by acting on it with piperidine. Piperic acid is reduced by sodium amalgam to  $\alpha$ - and  $\beta$ -dihydro-piperic acids, and when reduced catalytically it and its isomers are converted into tetrahydro-piperic acid (p. 369). It condenses with acetoacetic ester to give *methysticin* derivatives (p. 485) (*Borsche*, Ber. 60, 1138; *Lampe*, Bull. 43, 62). Its dilute solution gives piperonal and racemic acid with permanganate at 0° (*Doebner*, Ber. 23, 2372).

The constitution of piperic acid was established by *Fittig* and *Mielck* in 1874, and it was synthesised by *Ladenburg* and *Scholtz* in 1894 (Ber. 27, 2958).

**$\alpha$ -Methyl-piperic acid**, m.p. 208°, and  **$\alpha$ -ethyl-piperic acid**, m.p. 179°, have been synthesised by *Scholtz* (Ber. 28, 1187) by similar methods.

#### 14. Phenyl Triolefine Carboxylic Acids

**$\beta$ -Styryl-vinyl-crotonic acid**,  $\text{C}_6\text{H}_5\text{CH}:\text{CH} \cdot \text{CH}:\text{CH} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{CH}_3 \quad \text{COOH} \\ \quad \quad \text{H} \end{array}$ , m.p. 202–

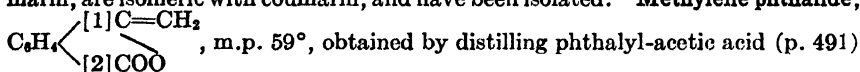
203°, is obtained through its ethyl ester from cinnamal-acetone and bromoacetic ester and zinc. The ester of an isomeric acid, m.p. 167–169°, is formed as a by-product (Kuhn, Ber. 65, 651).

#### IV. Compounds Which Can Be Regarded as the Oxidation Products of Mononuclear Aromatic Poly-alcohols with Unsaturated Side-chains

The chemistry of the aromatic poly-alcohols with unsaturated side-chains and their oxidation products has been studied even less than that of the corresponding saturated compounds. While a number of carboxylic acids and derivatives of this class is known, the alcohols and aldehydes from which they are theoretically derived are at present unknown. Consequently the compounds described in the following sections are not arranged strictly in a systematic order, although, in the main, the sequence is similar to that used in dealing with the oxidation products of aromatic poly-paraffin alcohols, pp. 372–398, 398–442.

##### 1. Phenylene Hydroxy-olefine Carboxylic Acids

The two possible *o*-vinyl alcohol benzoic acids are unknown in the free state. Their internal anhydrides or lactones, methylene phthalide and isocoumarin, are isomeric with coumarin, and have been isolated. **Methylene phthalide**,



gives a dibromide, m.p. 98°. **Dichloro-methylene phthalide**,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup [1] \text{C}=\text{CCl}_2 \\ \diagdown [2] \text{COO} \end{array}$ ,

m.p. 128°, and **tetrachloro-methyl phthalide**, m.p. 93°, are formed together when chlorine is passed into a mixture of acetic acid and phthalyl-chloroacetic acid (Zincke, Ann. 255, 383; 268, 294). **Bromo-methylene phthalide**, m.p. 133°, is obtained from acetophenone-*o*-carboxylic acid by the action of bromine. **Di-bromo-methylene phthalide**, m.p. 140°, is obtained from *o*-dibromo-acetophenone-*o*-carboxylic acid on heating with concentrated sulphuric acid. Derivatives of

**methylene-phthalimidine**,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup [1] \text{C}=\text{CH}_2 \\ \diagdown [2] \text{CO} \cdot \text{NR} \end{array}$ , are obtained by the action of

amines and amino-acids on *o*-acetophenone-carboxylic acid. **Nitromethylene-phthalide**,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{C}=\text{CHNO}_2 \\ \diagdown \text{CO} \cdot \text{O} \end{array}$ , m.p. 207° (decomp.), obtained from phthalic

anhydride and nitromethane, is decomposed by alkali into *nitrophenacyl-o*-carboxylic acid,  $\text{NO}_2\text{CH}_2\text{COC}_6\text{H}_4\text{COOH}$ , m.p. 121° (Gabriel, Ber. 29, 2518; 36, 570; 40, 83).

**Ethylidene-phthalide**,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup [1] \text{C}=\text{CH} \cdot \text{CH}_3 \\ \diagdown [2] \text{COO} \end{array}$ , forms orange-coloured crystals,

m.p. 64° (Gabriel, Ber. 19, 838; Gottlieb, Ber. 32, 958; Daube, Ber. 38, 206). **Propylidene-** and **isobutylidene phthalides**, b.p. 170° (12 mm.) and m.p. 97°, are obtained by condensing phthalic anhydride with the sodium salts and anhydrides of propionic and butyric acids, water and carbon dioxide being given off (Bromberg, Ber. 29, 1436). Under the influence of sodium ethylate these alkylidene phthalides isomerise to *diketo-hydrindenones* (q.v.). They are converted by caustic alkalis into *o*-keto-carboxylic acids (p. 383). Thus, ethylidene phthalide gives propiophenone-*o*-carboxylic acid. For their odours, see Berlingozzi, Gazz. 57, 264.

**Isocoumarin**,  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup [1] \text{CH}=\text{CH} \\ \diagdown [2] \text{CO} \cdot \text{O} \end{array}$ , m.p. 47°, b.p. 285°, is formed when silver

isocoumarin-carboxylate is distilled. It is readily volatile in steam. When heated with sodium carbonate it is converted into

**Anhydro-*o*-hydroxyvinyl-benzoic acid**,  $\text{O}(\text{CH}:\text{CH}[2]\text{C}_6\text{H}_4\text{COOH})_2$ , m.p. 183°,

which gives an anhydride,  $O(CH:CH[2]C_6H_4CO)_2O$ , m.p.  $234^\circ$ , with hydrogen chloride at  $160^\circ$ . Its imide,  $O(CH:CH[2]C_6H_4CO)_2NH$ , m.p.  $285^\circ$ , is obtained from the anhydride by the action of alcoholic ammonia at  $170^\circ$  (Bamberger,

Ber. 27, 207).  $\alpha$ -Chloro-isocoumarin,  $C_6H_4 \begin{matrix} [1]CH:CCl \\ [2]CO \cdot O \end{matrix}$ , m.p.  $99^\circ$ , a lachrymatory, is obtained from homophthalic anhydride, or its enol form, by the action of phosphorus pentachloride (Davies, J. 1928, 1616).

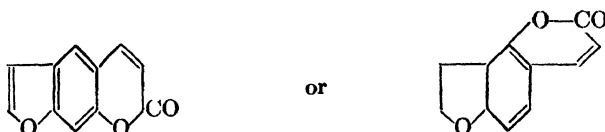
Isocarbostyryl,  $C_6H_4 \begin{matrix} [1]CH=CH \\ [2]CO-NH \end{matrix}$ , m.p.  $208^\circ$ , the lactam corresponding to isocoumarin, is isomeric with carbostyryl (p. 468). It is obtained by heating isocoumarin with alcoholic ammonia at  $130^\circ$ , or by heating isocarbostyryl-carboxylic acid (p. 492) or its silver salt. When distilled with zinc dust it gives isoquinoline (Vol. IV) (Bamberger, Ber. 27, 208).

$\alpha$ -Methyl-isocoumarin,  $C_6H_4 \begin{matrix} [1]CH=C \cdot CH_3 \\ [2]CO-O \end{matrix}$ , m.p.  $118^\circ$ , is obtained from

$\psi$ -diacetyl-cyano-benzyl cyanide,  $C_6H_4 \begin{matrix} [1]C(CN):C(OCOCH_3)CH_3 \\ [2]CN \end{matrix}$ , m.p.  $135^\circ$ ,

by the action of hydrogen chloride at  $180^\circ$ . The latter compound is the product of the action of acetic anhydride and sodium acetate on *o*-cyano-benzyl cyanide (Gabriel, Ber. 27, 831). A number of other homologues of isocoumarin have been prepared in a similar manner from *o*-cyano-benzyl cyanide, all of which readily give isocarbostyryls (cf. Harper, Ber. 29, 2543, et al.). Thus  $\alpha$ -methyl-isocoumarin gives  $\alpha$ -methyl-isocarbostyryl, m.p.  $211^\circ$ , with ammonia (Gabriel, Ber. 25, 3563). Methyl-isocoumarin gives methyl-benzyl-keto-*o*-carboxylic acid when boiled with caustic potash (p. 383).

Derivatives of coumarin with a furan ring attached to the benzene ring have been extracted from *Citrus bergamia*, *Fagara xanthoxyloides*, *Pimpinella saxifraga*, and other plants. They contain the following carbon skeleton:



They are therefore *coumarin* and *coumarone* derivatives at the same time. A number of compounds of this class, viz., *bergapten*, *isobergapten*, (*iso*-)*pimpinelline*, *xanthotoxine*, (*iso*-)*imperatorine*, (*hydroxy*-)*peucedanine*, *oreosolone*, and *ostruthole*, and their degradation products have been dealt with in Vol. II, p. 497.

## 2. Phenylene Aldehydo-carboxylic Acids

*p*-Aldehydo-cinnamic acid,  $CHO[4]C_6H_4CH:CHCOOH$ , m.p.  $247^\circ$ , has been obtained from terephthalaldehyde by Perkin's reaction (p. 462) (L6w, Ann. 231, 375).

## 3. Phenylene Dicarboxylic Acids

*o*-Carboxy-cinnamic acid,  $COOH[2]C_6H_4CH:CHCOOH$ , melts at  $174^\circ$ , changing to phthalide-acetic acid (p. 439) from which it can be obtained by heating with alkali (cf. Leupold, Ber. 34, 2832). It is also formed by the careful oxidation of  $\beta$ -naphthol with permanganate while on further oxidation it is converted into *o*-carboxyphenyl-glyoxylic acid (p. 440) (Ehrlich, Mo. 9, 527).

*o*-Cyano-cinnamic acid,  $CN[2]C_6H_4CH:CHCOOH$ , m.p.  $252^\circ$ , is obtained from *o*-cyano-benzylidene chloride by the action of sodium acetate and acetic anhydride, or from *o*-amino-cinnamic acid (Drory, Ber. 24, 2574; Komppa, Ber. 27, R 262). It is also formed by a peculiar reaction, when the sodium salt of  $\alpha$ -

nitroso- $\beta$ -naphthol,  $\text{C}_6\text{H}_7$   $\begin{array}{c} \text{C(NO):C(OH)} \\ | \\ \text{CH=CH} \end{array}$ , is heated to  $250^\circ$  (Ger. Pat. 116,123).

*p*-Carboxy-cinnamic acid, does not melt, but sublimes. It is obtained from terephthalaldehydic carboxylic ester by the action of sodium acetate and acetic anhydride (Löw, Ann. 231, 369).

*o*-Phenylene-diacrylic acid,  $\text{C}_6\text{H}_4[1,2](\text{CH}:\text{CH}\cdot\text{COOH})_2$ , m.p. above  $300^\circ$ , is obtained from *o*-xylylene-dichloro-dimalonic ester by the action of alcoholic potash, or from *o*-phthalaldehyde by Perkin's reaction (Perkin, Ber. 19, 435; Thiele, Ann. 347, 117). *p*-Phenylene-diacrylic acid is obtained from *p*-aldehydo-cinnamic ester, or terephthalaldehyde, sodium acetate and acetic anhydride (Löw, Ann. 231, 375; Ephraim, Ber. 34, 2784), or from *p*-xylylene-dibromo-dimalonic ester.

#### 4. Phenyl Olefine Ketols

Hydroxymethylene-acetophenone,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}:\text{CHOH}$ , when liberated from its sodio-compound, is a rather unstable oil. Its sodio-compound is obtained by the action of sodium ethylate and ethyl formate on acetophenone. This compound was formerly thought to be benzoyl-acetaldehyde (p. 408). For the constitution of hydroxymethylene compounds, see Vol. I, p. 396. Its sodio-compound gives a mixture of *imino-bis-formyl-acetophenone*,  $\text{NH}(\text{CH}:\text{CH}\cdot\text{COC}_6\text{H}_5)_2$ , and 2-phenyl-5-benzoyl-pyridine (Vol. IV) when treated with ammonia (Benary, Ber. 57, 828; 59, 108; 60, 914; 61, 2252). With phenyl isocyanate it gives an *O*-carbanilido derivative, m.p.  $125^\circ$ , which readily isomerises under the action of potassium carbonate to *C*-carbanilide, m.p.  $94^\circ$  (Dieckmann, Ber. 37, 4631). With phenylhydrazine it is converted into diphenyl-pyrazole (Vol. IV) and with hydroxylamine into benzoyl-acetaldoxime (p. 408). On catalytic reduction it gives  $\alpha$ -phenyl-allyl alcohol (p. 456). See also benzylidene-phenoxy-acetone, p. 460.

#### 5 and 6. Phenyl-hydroxy-olefine- and Phenyl-diolefine-carboxylic Acids

Hydroxymethylene-phenyl-acetic ester,  $\text{C}_6\text{H}_5\text{C}(\text{COOC}_2\text{H}_5):\text{CHOH}$ , see formyl-phenyl-acetic ester, p. 422.

$\beta$ -Methoxy-cinnamic ester,  $\text{C}_6\text{H}_5\text{C}(\text{OCH}_3):\text{CHCOOC}_2\text{H}_5$ , b.p.  $155^\circ$  (14 mm.), and  $\beta$ -ethoxy-cinnamic ester, b.p.  $168^\circ$  (16 mm.), are obtained from phenyl-propionic ester (p. 479) by the action of sodium ethylate, and from benzoyl-acetic ester and ethyl orthoformate. The corresponding acids melt at  $180^\circ$  and  $162^\circ$  with evolution of carbon dioxide and formation of  $\beta$ -phenyl-vinyl-methyl and ethyl ethers (p. 456) (Claisen, Ber. 29, 1005; Moureu, C.r. 138, 206, 286).  $\beta$ -Phenoxy-cinnamic ester,  $\text{C}_6\text{H}_5\text{C}(\text{OC}_6\text{H}_5):\text{CHCOOC}_2\text{H}_5$ , m.p.  $76^\circ$ , b.p.  $265^\circ$  (10 mm.), is obtained by adding on sodium phenate to phenyl-propionic acid (p. 479); the free acid, m.p.  $143^\circ$ , loses carbon dioxide on heating and is converted into  $\alpha$ -phenoxy-styrene,  $\text{C}_6\text{H}_5\text{C}(\text{OC}_6\text{H}_5):\text{CH}_2$  (Ruhemann, J. 79, 918, 1185).  $\alpha$ -Phenoxy-cinnamic acid,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{OC}_6\text{H}_5)\text{COOH}$ , m.p.  $181^\circ$ , is obtained synthetically from benzaldehyde, sodium phenoxy-acetate and acetic anhydride, or from benzylidene-phenoxy-acetone (page 460) by the action of sodium hypochlorite. When heated it partly decomposes into carbon dioxide and  $\omega$ -phenoxy-styrene, and partly into carbon monoxide and phenyl phenylacetate (Stoermer, Ber. 35, 3555; 38, 1958).

$\gamma$ -Phenyl- $\alpha$ -hydroxy- $\Delta^2$ -crotonic acid, styryl- $\alpha$ -hydroxyacetic acid,  $\text{C}_6\text{H}_5\text{CH}:\text{CH}\cdot\text{CH}(\text{OH})\text{COOH}$ , m.p.  $137^\circ$ , is obtained by the hydrolysis of its nitrile, cinnamaldehyde cyanhydrin, m.p.,  $74^\circ$ , with cold concentrated hydrochloric acid, or by the reduction of cinnamoyl-formic acid (p. 486) with sodium amalgam. When it is boiled with hydrochloric acid it changes smoothly to benzoyl-propionic acid (p. 431) (Erlenmeyer, Ber. 37, 3124), while boiling caustic alkali converts it into benzyl-pyruvic acid (p. 429). Benzyl-propionic acid, when heated alone

or with acetic anhydride, gives  $\gamma$ -phenyl- $\Delta^2$ -crotonolactone,  $\text{C}_6\text{H}_5\text{C}:\text{CH}\cdot\text{CH}_2\text{COO}$ ,



is opened by sodium hydroxide or ethylate, **isomethysticin**, or **methysticinic acid**,  $(\text{CH}_2\text{O})_2\text{C}_6\text{H}_5\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{C}(\text{OCH}_3):\text{CHCOOH}$ , m.p. 191–192°, being formed. With methyl alcoholic potash, the enol-ether group opens and the molecule rearranges becoming a  $\beta$ -keto-acid  $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOH}$  (*Borsche*, Ber. 60, 982, 1135, 2113; 62, 360). Similar treatment of  $\psi$ -methysticin gives rise to methysticinic acid m.p. 184.5°.

### 9. Phenyl Dihydroxy-olefine Carboxylic Acids

**Hydroxymethylene-phthalide**  $\text{C}_6\text{H}_4\begin{matrix} \swarrow [1]\text{C}=\text{CHOH} \\ \searrow [2]\text{CO}\cdot\text{O} \end{matrix}$ , m.p. 148°, is obtained by

boiling  $\omega$ -bromoacetophenone-*o*-carboxylic acid with water. It reacts with hydroxylamine and phenylhydrazine in its tautomeric form of a formyl phthalide, an oxime, m.p. 152° and a phenylhydrazone, m.p. 180° (decomp.), being formed (*Gabriel*, Ber. 40, 74).

### 10. Phenyl Olefine- and 11. Phenyl Diolefine- $\alpha$ -keto-carboxylic Acids

These are obtained by the condensation of aromatic aldehydes with pyruvic acid. **Cinnamoyl-formic acid**, **benzylidene-pyruvic acid**,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{COOH}$ , is known in two forms. One is obtained from benzaldehyde and pyruvic acid using hydrochloric acid as condensing agent. It is usually obtained as an oil, which crystallises with m.p. 62–63° (*Musajo*, Gazz. 62, 901); with 1  $\text{H}_2\text{O}$  it melts at 53–54°. The other form is obtained when caustic soda, or methyl alcoholic potash in the cold is used as condensing agent and forms shining leaflets containing 1  $\text{H}_2\text{O}$ , m.p. 53–54°, and anhydrous, m.p. 61–62°. It crystallises from benzene with benzene of crystallisation, m.p. 70–76° (*Friedmann*, Helv. 14, 783; *Reimer*, Am. 46, 783; 48, 2454; 53, 3147). The acid is reduced by sodium amalgam to  $\gamma$ -phenyl- $\alpha$ -hydroxy-crotonic acid (p. 484) (*Erlenmeyer*, Ber. 36, 2527). The esters are known in two forms, the *methyl ester* occurring as a red oil and as yellow needles, m.p. 73°. The syrupy form of the acid is also obtained from its nitrile, **cinnamoyl cyanide**,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CN}$ , m.p. 114° (*Clausen*, Ber. 14, 2472). Phenylhydrazone, m.p. 163–165° (*Ciusa*, Gazz. 49, I, 164). Its dibromide, m.p. 142°, gives colourless needles of  $\beta$ -bromo-benzylidene-pyruvic acid, m.p. 131–132°, on boiling with water (*Reimer*, Am. 48, 2454).

***o*-Nitrocinnamoyl-formic acid**,  $\text{NO}_2[2]\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{COOH}$ , m.p. 135°, is obtained from *o*-nitrobenzaldehyde and pyruvic acid. When treated with alkali, even in the cold, it loses oxalic acid, and is converted into *indigo*.

**Cinnamal-pyruvic acid**,  $\text{C}_6\text{H}_5\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{COOH}$ , forms red crystals, m.p. 73°, slowly changing to yellow crystals, m.p. 104°. It is obtained from cinnamaldehyde and pyruvic acid in weakly alkaline solution (*Lubrzynska*, Biochem. J. 7, 37). It is reduced by sodium amalgam to the corresponding  $\alpha$ -hydroxy-acid, and this is converted into  $\delta$ -benzylidene-laevulinic acid (p. 488) on boiling with hydrochloric acid (*Erlenmeyer*, Ber. 37, 1318).

**3,4-Methylene-dioxy-cinnamoyl-formic acid**,  $(\text{CH}_2\text{O})_2[3,4]\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{COOH}$ , m.p. 149°, and **3,4-methylene-dioxy-cinnamoyl-pyruvic acid**,  $(\text{CH}_2\text{O})_2[3,4]\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{COOH}$ , m.p. 166°, are obtained from piperonal and piperonyl-acrolein (p. 459), respectively.

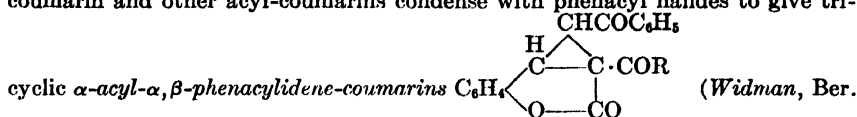
### 12. Phenyl Olefine $\beta$ -Keto-carboxylic Acids

These are obtained by condensing acetoacetic ester and aromatic aldehydes either by means of gaseous hydrogen chloride or, better, by means of primary or secondary amines in the cold.  **$\alpha$ -Benzylidene-acetoacetic ester**,  $\text{C}_6\text{H}_5\cdot\text{CH}:$

$\begin{matrix} \swarrow \text{COOC}_2\text{H}_5 \\ \searrow \text{COCH}_3 \end{matrix}$ , m.p. 59°, b.p. 181° (17 mm.) (*Knoevenagel*, Ber. 29, 172; Ann.

281, 63). ***m*-Nitro ester**, m.p. 112° (*Biginelli*, Gazz. 23, I, 360).  **$\gamma$ -Benzylidene-diethyl-acetoacetic ester**,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COC}(\text{C}_2\text{H}_5)_2\cdot\text{COOC}_2\text{H}_5$ , m.p. 101°.

**Acetyl-coumarin**,  $C_6H_5$   $\left\{ \begin{array}{l} [1]CH:C \cdot COCH_3 \\ [2]O \text{---} C:O \end{array} \right.$ , m.p. 124°, obtained from acetoacetic ester and salicylaldehyde in the presence of acetic anhydride, is slightly acidic (cf. coumarin and nitro-coumarin, p. 474) (*Widman*, Ber. 35, 1153; *Knoevenagel*, Ber. 37, 4497). See also acetyl-hydroxy-coumarin, p. 491. Acetyl coumarin and other acyl-coumarins condense with phenacyl halides to give tri-



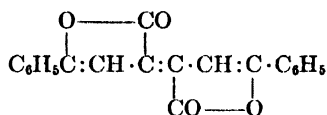
**Allyl-benzoyl-acetic ester**,  $C_6H_5 \cdot CO \cdot CH(CH_2 \cdot CH:CH_2) \cdot COOC_2H_5$ , m.p. 122° (*Baeyer*, Ber. 16, 2132). **Methyl-γ-cinnamal-acetoacetate**, *allokawain*,  $C_6H_5CH:CH \cdot CH:CHCOCH_2COOCH_3$ , m.p. 93°, is obtained by condensing cinnamal-acetyl chloride with methyl sodio-acetoacetate, followed by removal of the acetyl group with aqueous ammonia. For **methyl 3,4-methylene-dioxy-cinnamal-acetoacetate**, *allomethysticin*,  $CH_2O_2[3,4]C_6H_5CH:-CH:CH:CHCOCH_2COOCH_3$ , m.p. 135-137°, see p. 485 (*Borsche*, Ber. 60, 1138, 2120).

**γ-Phenyl-α-acetyl-crotonolactone**,  $C_6H_5C:CH \cdot CH(COCH_3)COO$ , m.p. 113°, is obtained from acetophenone-acetoacetic ester (p. 434) on boiling with alcoholic potash (*Borsche*, Ber. 39, 1809).

### 13. Phenyl Olefine and Phenyl Diolefine γ-Keto-carboxylic Acids

These are condensation products of (1) aldehydes and γ-keto-carboxylic acids with acids or alkalis, or (2) olefine-dicarboxylic anhydrides, such as maleic or citraconic anhydrides, and benzene hydrocarbons with aluminium chloride.

**β-Benzoyl-acrylic acid**,  $C_6H_5 \cdot CO \cdot CH:CH \cdot COOH$ , *trans* m.p. 97°, anhydrous; *cis*-form unknown. It is obtained from maleic anhydride (see above); by the action of phenyl-γ-keto-α-hydroxybutyric acid (p. 433) on sulphuric acid; by the action of potassium acetate on bromobenzoyl-propionic acid; and by the action of sodium hypiodite on styryl-acetic acid (*Bougault*, C.r. 146, 140; Ann. ch. ph. [8] 15, 491). Its esters isomerise in the light. *Methyl ester*, m.p. 34°; isomeric ester, m.p. 67° (*Rice*, Am. 45, 222). The acid on boiling with acetic anhydride loses water and forms first the enol,  $C_6H_5C(OH):C:CHCOOH$ , and then the corresponding lactone, and finally dimerises to a *trans*-dilactone, **diphenacyl-fumaric dilactone**:



This compound, known as *Pechmann's dye*, consists of red plates with a bronze lustre, which sublime on heating and give diphenyl-acyl-fumaric acid (the keto- and the enol-form) when decomposed by caustic potash (*Boger*, Proc. Wash. 10, 363; Am. 46, 2871). **Trichloro-ethylidene-acetophenone**,  $C_6H_5 \cdot CO \cdot CH:CH \cdot CCl_3$ , m.p. 102°, is obtained from chloral-acetophenone (p. 433) by the action of sulphuric acid. **β-Benzoyl-crotonic acid**,  $C_6H_5 \cdot CO \cdot C(CH_3):CH \cdot COOH$ , m.p. 113°, is obtained from citraconic anhydride (*Pechmann*, Ber. 15, 891; *Mayer*, Ber. 56, 1424).

**β-Benzylidene-laevulinic acid**,  $C_6H_5 \cdot CH:C \begin{array}{l} CH_2 \cdot COOH \\ CO \cdot CH_3 \end{array}$ , m.p. 125°, is obtained by condensing benzaldehyde with laevulinic acid in acid solution. It is converted into 3-acetyl-1-naphthol on distillation, into phenyl-itaconic acid on oxidation, and into β-benzyl-laevulinic acid (p. 432) on reduction. With hydroxyl-

amine it gives **benzylidene-laevoxime**,  $C_6H_5CH:C \begin{array}{l} CH_2 \cdot CO \cdot O \\ C(CH_3)=N \end{array}$ , m.p. 94



**$\delta$ -Benzylidene-laevulinic acid**,  $C_6H_5 \cdot CH:CH \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$ , m.p.  $120^\circ$ , is obtained by condensing benzaldehyde and laevulinic acid in alkaline solution. When distilled it gives benzylidene-angelica lactone, m.p.  $90^\circ$  (Erdmann, Ber. 24, 3202).

**$\delta$ -Cinnamal-laevulinic acid**,  $C_6H_5CH:CH \cdot CH:CH:CH \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$ , m.p.  $161^\circ$ , forms sulphur yellow crystals, and is obtained by condensing cinnamaldehyde and laevulinic acid in the presence of pyridine (Rupe, Ber. 38, 1113).

#### 14. Phenylhydroxy-olefine- $\gamma$ -keto-carboxylic Acids

**Cinnamoyl-lactic acid** is a representative of this group. Its ethyl ester,  $C_6H_5CH:CH \cdot COCH_2 \cdot CHOH \cdot COOC_2H_5$ , b.p.  $173^\circ$  (6 mm.), is obtained from cinnamoyl chloride and ethyl lactate in the presence of pyridine (Sabetay, Bull. 47, 436).

#### 15. Phenyl Olefine- $\alpha$ , $\gamma$ -diketo-carboxylic Acids

**Cinnamoyl-pyruvic acid**,  $C_6H_5CH:CH \cdot CO \cdot CH_2COCOOH$ , forms bright yellow needles, m.p.  $139-140^\circ$ . Its ethyl ester, m.p.  $70^\circ$ , is obtained from benzylidene-acetone and ethyl oxalate in the presence of sodium. One molecule of the ester combines with hydroxylamine to form an isoxazole ring (Ryan, Irish, Ac. 1913).

#### 16. Phenyl Olefine- and 17. Phenyl Diolefine-dicarboxylic Acids

**Benzylidene-malonic acid**,  $C_6H_5CH:C(COOH)_2$ , melts with the formation of cinnamic and allocinnamic acid (p. 465). It is obtained from benzaldehyde and malonic acid in the presence of acetic acid. A mixture of benzylidene-aniline or similar compounds with malonic acid, gives cinnamic acid on heating (Knoevenagel, Ber. 31, 2596). Its ethyl ester, b.p.  $198^\circ$  (13 mm.), is obtained from benzaldehyde and malonic ester in the presence of hydrochloric acid or amines. It enters into addition reactions much more readily than the free acid. Its methyl ester gives methyl  $\beta$ -anilino-benzyl malonate, m.p.  $117^\circ$ , with aniline, and methyl  $\beta$ -phenylhydrazino-benzyl malonate, m.p.  $94^\circ$ , with phenylhydrazine (Goldstein, Ber. 29, 813). With substituted benzaldehydes, substituted benzylidene-malonic acids are obtained, such as *o*-nitro-benzylidene-malonic acid, which is reduced by ferrous sulphate and ammonia to  $\beta$ -carbostyryl-carboxylic acid (Stuart, J. 53, 140; Knoevenagel, Ber. 31, 2596).  **$\alpha$ -Cyano-cinnamic acid**,

$C_6H_5CH:C \begin{matrix} \nearrow COOH \\ \searrow CN \end{matrix}$ , m.p.  $180^\circ$ , is obtained from benzaldehyde and cyanoacetic

acid on warming, or from benzaldehyde and cyanoacetyl chloride on rapid boiling. It is converted into cinnamonitrile (p. 465) on heating. Methyl ester, m.p.  $70^\circ$ ; ethyl ester, m.p.  $50^\circ$ . A number of semi-nitriles of similarly constituted aromatic malonic acids have been obtained by combining the more accessible aromatic aldehydes with cyanoacetic acid (Komppa, Ber. 27 R, 262). The dinitrile, diamide, and nitrile-amide of benzylidene-malonic acid, m.p.  $87^\circ$ ,  $190^\circ$ , and  $23^\circ$ , respectively, have also been synthesised by condensing benzaldehyde with malono-nitrile, malonamide, and cyanacetamide (Heuck, Ber. 28, 2251; Walter, Ber. 35,

1320). **Benzylidene-barbituric acid**,  $C_6H_5 \cdot CH:C \begin{matrix} \nearrow CO \cdot NH \\ \searrow CO \cdot NH \end{matrix} CO$ , is readily obtained by condensing benzaldehyde with malonyl-urea (Conrad, Ber. 34, 1340).

**Carbostyryl- $\alpha$ -carboxylic acid**,  $C_6H_5 \begin{matrix} \nearrow [1]CH:C \cdot COOH \\ \searrow [2]NH \cdot CO \end{matrix}$ , is obtained from *o*-amino-benzaldehyde and malonic acid at  $120^\circ$ , or from *o*-nitro-benzylidene-malonic acid (see above) (Stuart, J. 53, 140). Its silver salt gives carbostyryl when heated.

**Coumarin- $\alpha$ -carboxylic acid**,  $C_6H_4 \begin{matrix} \nearrow [1]CH:C \cdot COOH \\ \searrow [2]O \cdot C:O \end{matrix}$ , m.p.  $187^\circ$ , decomposes into carbon dioxide and coumarin at  $290^\circ$ . This compound is obtained from salicylaldehyde and malonic acid in the presence of acetic acid or amines (Knoeven-

nagel, Ber. 31, 2593). It has also been obtained from  $\alpha$ -cyano-coumarin,

$\text{C}_6\text{H}_4 \begin{cases} [1] \text{CH} : \text{C} \cdot \text{CN} \\ [2] \text{O} - \text{CO} \end{cases}$ , m.p.  $182^\circ$ , a condensation product of salicylaldehyde and

ethyl cyanoacetate (Bechert, J. pr. 50, 1).  $\alpha$ -Coumarin-carboxylic amide, m.p.  $269^\circ$ ; anilide, m.p.  $250^\circ$  (Ger. Pat. 172,724); cf. ethyl  $\beta$ -hydroxy-coumarin- $\alpha$ -carboxylate (p. 491).

**Cinnamal-malonic acid**, *phenyl-butadiene-dicarboxylic acid*,  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} : \text{CH} : \text{C}(\text{COOH})_2$ , m.p.  $208^\circ$ , is obtained from cinnamaldehyde, calcium malonate, and acetic acid (Staudinger, Ber. 56, 699). It is yellow, but dimerises and becomes colourless when exposed to light. The dimeric modification is oxidised to  $\alpha$ -truxillic acid (Vol. II, p. 41) and possibly, like this compound, contains a cyclobutane ring. With concentrated sulphuric acid, the monomolecular form is regenerated. When heated, the dimeric acid gives a dimeric cinnamal-acetic acid, m.p.  $204^\circ$  (Koehler, Am. Ch. J. 28, 235; Riiber, Ber. 35, 2411; 46, 335). Monomolecular cinnamal-malonic acid loses carbon dioxide on heating and gives a mixture of stereoisomeric cinnamal-acetic acids (p. 480). Methyl and ethyl esters m.p.  $67^\circ$  and  $36^\circ$ . When reduced with sodium amalgam it gives 1,4-hydrocinnamal-malonic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH} : \text{CH} : \text{CH}(\text{COOH})_2$ , m.p.  $107^\circ$  (decomp.). When this is heated with caustic soda it changes to 3,4-hydrocinnamal-malonic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH} : \text{C}(\text{COOH})_2$ , m.p.  $116^\circ$  (decomp.) (Thiele, Ann. 306, 259). When the reduction is carried out catalytically, gradual hydrogenation does not take place, but  $\omega$ -phenyl-*n*-propyl-malonic acid, m.p.  $98^\circ$ , is the only product (Paal, Ber. 45, 2221). Cinnamal-cyanacetic acid,  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} : \text{CH} : \text{C}(\text{CN})\text{COOH}$ , m.p.  $212^\circ$ , forms a stable and an unstable ethyl ester, both melting at  $113^\circ$  (Reimer, Am. Ch. J. 50, 157). 3,4-Methylene-dioxy-cinnamal-malonic acid,  $(\text{CH}_2\text{O}_2)[3,4]\text{C}_6\text{H}_3\text{CH} : \text{CH} : \text{CH} : \text{C}(\text{COOH})_2$ , melts at  $223^\circ$ , decomposing into carbon dioxide and isopiperic acid (p. 481) (Ott, Ber. 55, 2662).

**Phenyl-allyl-malonic acid**,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_2\text{CH} : \text{CH}_2)(\text{COOH})_2$ , m.p.  $145^\circ$  (decomp.), has been obtained in the form of its ester by the action of allyl iodide on ethyl phenyl-malonate (Wislicenus, Ber. 29, 2600).

$\text{CH} : \text{COOH}$

**Phenyl-maleic acid**,  $\text{C}_6\text{H}_5 \cdot \text{C} : \text{COOH}$ , forms an anhydride, m.p.  $119^\circ$ , at less than  $100^\circ$ . This anhydride is also obtained, together with phenyl-maleic acid, when the reaction product of phenyl-succinic acid and bromine or phosphorus bromide is treated with water (Alexander, Ann. 258, 67).

**Phenethyl-fumaric acid**, m.p.  $202^\circ$ , and **phenethyl-maleic acid**, m.p.  $104^\circ$  (anhydride, m.p.  $74^\circ$ ), are both obtained from acetone and benzyl-pyruvic acid, which combine to form acetone-benzyl-pyruvic acid. This is dehydrated and converted into an acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 \cdot \text{C}(\text{COOH}) : \text{CH} : \text{COCH}_3$ , which is oxidised with sodium hypochlorite. The two acids are separated by means of their sodium hydrogen salts (Cordier, C.r. 186, 869).

**Coumarin- $\alpha$ -acetic acid**,  $\text{C}_6\text{H}_4 \begin{cases} \text{CH} : \text{C} \cdot \text{CH}_2\text{COOH} \\ \text{O} - \text{CO} \end{cases}$ , m.p.  $150^\circ$ , is obtained

from salicylaldehyde, succinic anhydride and sodium succinate at  $170$ – $180^\circ$ .  $\alpha,\alpha$ -Dicoumarin, m.p.  $315^\circ$ , is obtained at the same time. It can also be obtained from phenol and hydroxymethylene-succinic ester in the presence of sulphuric acid (Dey, Indian J. 8, 817).

**Coumarin- $\beta$ -carboxylic acid**,  $\text{C}_6\text{H}_4 \begin{cases} \text{C}(\text{COOH}) : \text{CH} \\ \text{O} - \text{CO} \end{cases}$ , m.p.  $180^\circ$ . When its

silver salt is distilled it decomposes into carbon dioxide and coumarin. Its ethyl ester, m.p.  $78^\circ$ , is obtained from phenol and oxalacetic ester in the presence of sulphuric acid. Resorcinol and oxalacetic ester in the presence of sodium ethylate give umbelliferone- $\beta$ -carboxylic acid, *resorcylic-maleic lactone*,

$\text{HO}[4]\text{C}_6\text{H}_3 \begin{cases} \text{C}(\text{COOH}) : \text{CH} \\ \text{O} - \text{CO} \end{cases}$ , m.p.  $248^\circ$  (Pechmann, Ber. 34, 381, 422).

For two coumarin- $\beta$ -acetic acids, substituted in the benzene nucleus,

$\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{C}(\text{CH}_2\text{COOH}) : \text{CH} \\ \diagdown \text{O} \quad \text{CO} \end{array}$  and the unstable  $\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{C}(:\text{CHCOOH}) \cdot \text{CH}_2 \\ \diagdown \text{O} \quad \text{CO} \end{array}$ , which are obtained from phenols and acetone-dicarboxylic acid, see *Dey*, J. 107, 1606.

**BENZYLIDENE-SUCCINIC ACIDS.** Phenyl-itaconic acid,  $\text{C}_6\text{H}_5\text{CH}$

$\text{HOOC} \cdot \text{CH}_2 \cdot \text{C}(\text{COOH}) \cdot \text{CH}$ , m.p. 192° (decomp.). Dimethyl ester, b.p. 186° (19 mm.) is obtained (1) from ethyl succinate and benzaldehyde with sodium ethylate (*Hecht*, Mo. 24, 367); (2) from phenyl-paraconic ester with sodium ethylate, or better, in both cases, with sodium in ether (*Cordier*, Ann. ch. [10], 15, 228). When heated with acetic anhydride (*Dieckmann*, Ber. 47, 1435), or when fused, preferably in a vacuum, it loses water and forms its anhydride, m.p. 165°. This, every time it is fused, isomerises to a slight extent to phenyl-citraconic anhydride, m.p. 60° (*Fittig*, Ann. 305, 26, 49), and this, with water, gives phenyl-citraconic acid, m.p. 105-108°. When phenyl-citraconic acid is dissolved in chloroform containing a little bromine, and exposed to light, it rearranges to phenyl-mesaconic acid, m.p. 212°.

A fourth isomer, phenyl-aticonic acid,  $\text{HOOC} \cdot \text{C}(\text{CH}_2\text{COOH}) \cdot \text{CH}$ , m.p. 149-151°, which is stereoisomeric with phenyl-itaconic acid, is formed partially when any of the three preceding compounds is boiled with aqueous caustic soda. With conc. sulphuric acid, phenyl-itaconic acid merely gives an anhydride, but phenyl-aticonic acid readily loses water and is converted into  $\alpha$ -indone-acetic acid,  $\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{CH} \\ \diagdown \text{CO} \end{array} \text{C} \cdot \text{CH}_2\text{COOH}$ . This is regarded as evidence of

the cis-position of phenyl and carboxyl groups in phenyl aticonic acid (cf. Vol. I, p. 571, and *Fittig*, Ann. 304, 130; 305, 35; 330, 292; *Stobbe*, Ber. 41, 3983).

Coumarin- $\alpha$ -propionic acid,  $\text{C}_6\text{H}_5 \begin{array}{c} \diagup [1] \text{CH} = \text{C} \cdot \text{CH}(\text{CH}_3)\text{COOH} \\ \diagdown [2] \text{O} - \text{CO} \end{array}$ , m.p. 171°, is

obtained together with *o*-hydroxyphenyl-methyl-isocrotonic acid by the condensation of salicylaldehyde and sodium pyrotartrate in the presence of acetic anhydride. When distilled it readily forms  $\alpha$ -ethyl-coumarin (*Fittig*, Ann. 255, 285).

Methyl-phenyl-itaconic acid,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3) = \text{C}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}$ , m.p. 171° (decomp.), is obtained by condensing ethyl succinate with acetophenone in ether solution with sodium ethylate as condensing agent. Anhydride, m.p. 114°. It isomerises in different ways, like phenyl-itaconic acid (see above) (*Stobbe*, Ber. 37, 1619).

Styryl-succinic acid,  $\text{C}_6\text{H}_5\text{CH} : \text{CH} \cdot \text{CH}(\text{COOH})\text{CH}_2\text{COOH}$ , m.p. 173°, is obtained from cinnamylidene-malonic ester by the action of alcoholic potassium cyanide, followed by hydrolysis of the reaction product (cf. phenyl-succinic acid, p. 435, and *Thiele*, Ann. 306, 254).

Cinnamal-succinic acid,  $\text{C}_6\text{H}_5\text{CH} : \text{CH} \cdot \text{CH} \cdot \text{C}(\text{COOH})\text{CH}_2\text{COOH}$ , m.p. 215-218° (decomp.), is obtained from cinnamaldehyde and ethyl succinate, using sodium ethylate as condensing agent. It is reduced by sodium amalgam to phenethylidene-pyrotartaric acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH} : \text{CHCH}(\text{COOH})\text{CH}_2\text{COOH}$ , which, when boiled with caustic soda, changes to phenethyl-itaconic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 \cdot \text{CH} : \text{C}(\text{COOH}) \cdot \text{CH}_2\text{COOH}$ , m.p. 153° (*Fichter*, Ber. 34, 2188; but cf. *Fittig*, Ann. 331, 151).

Phenyl-hydroxymaleic anhydride,  $\text{C}_6\text{H}_5\text{C} : \text{C}(\text{OH})\text{CO} \cdot \text{O} \cdot \text{CO} + 1\text{H}_2\text{O}$ , m.p. <100°, and 163° (anhydrous), is obtained by the action of cold sulphuric acid on phenyl-oxalacetic or  $\alpha$ -cyanophenyl-pyruvic ester. It decomposes slowly in the cold and more rapidly on warming into phenyl-pyruvic acid and carbon dioxide. If it is warmed with alcohols, esters of phenyl-pyruvic acid are formed (*Bougault*, C.r. 162, 760).

$\beta$ -Phenyl-glutaconic acid,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_2\text{COOH}) : \text{CHCOOH}$ , m.p. 154°, is obtained from the condensation product of phenyl-propionic ester with sodio-malonic ester; its ester b.p. 187° (11 mm.). With ammonia it gives  $\gamma$ -phenyl- $\alpha, \alpha'$ -dihydroxypyridine (*Ruhemann*, J. 75, 245; *Michael*, J. pr. 49, 20; *Feist*, Ann. 370, 72; 428, 40).

**$\beta$ -(*p*-Methoxyphenyl)-glutaconic acid**,  $\text{CH}_3\text{O}[4]\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}_2\text{COOH})\text{:CH}\cdot\text{COOH}$ , m.p.  $176^\circ$ , is obtained by condensing anisole with acetone-dicarboxylic acid. Its *anhydride*, m.p.  $160^\circ$ , is obtained when the acid is heated to  $180^\circ$ , or boiled with acetic anhydride. On boiling with  $\text{HCl}$  it gives *p*-isopropenyl-anisole (p. 451) (*Limaye*, Indian, 8, 137).

**$\alpha$ -Benzylidene-glutaric acid**,  $\text{C}_6\text{H}_5\text{CH}\text{:C}(\text{COOH})\text{CH}_2\text{CH}_2\text{COOH}$ , m.p.  $177^\circ$  (*Fittig*, Ann. 282, 338; *Fichter*, Ber. 31, 2004).

**$\alpha$ -Benzyl-glutaconic acid**,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{COOH})\text{CH}\text{:CHCOOH}$ , m.p.  $145^\circ$  (*Conrad*, Ann. 222, 261). The ethyl ester, b.p.  $203^\circ$  (10 mm.), gives *benzyl-dihydroxyppyridine* with aqueous ammonia at  $100^\circ$  (*Ruhemann*, J. 63, 259).  **$\beta$ -Styryl-glutaric acid**,  $\text{C}_6\text{H}_5\text{CH}\text{:CH}\cdot\text{CH}(\text{CH}_2\text{COOH})_2$ , m.p.  $135^\circ$ , is obtained from the condensation product of  $\beta$ -styryl-acrylic ester and sodio-malonic ester, or by the oxidation of  $\beta$ -styryl-dihydroresorcinol (Vol. II, p. 112) with sodium hypochlorite (*Vorlander*, Ann. 345, 206).

### 18. Phenyl Olefine Tricarboxylic Acids

**Ethyl-phenyl-carboxy-aconitate**,  $\text{C}_6\text{H}_5\text{C}(\text{COOC}_2\text{H}_5)_2\text{C}(\text{COOC}_2\text{H}_5)\text{:CHCOO}\cdot\text{C}_2\text{H}_5$ , and **benzyl-carboxy-aconitate** are obtained from phenyl and benzyl-malonic esters by the action of ethyl chlorofumarate (*Ruhemann*, J. 81, 1212).

### 19. Phenylhydroxy-olefine Dicarboxylic Acids

**$\beta$ -Styryl-paraconic acid**,  $\text{C}_6\text{H}_5\text{CH}\text{:CH}\cdot\text{CH}\cdot\text{CH}(\text{COOH})\text{CH}_2\cdot\text{COO}$ , m.p.  $145^\circ$ , obtained from cinnamic aldehyde and succinic acid, gives  $\beta$ -styryl-crotonic acid (p. 481) on boiling with water (*Bougault*, C.r. 142, 153).

**Ethyl  $\beta$ -hydroxy-coumarin- $\alpha$ -carboxylate**, or  **$\alpha$ -carbethoxy-benzotetronic acid**,  $\text{C}_6\text{H}_5\text{C}(\text{OH})\text{:CH}\cdot\text{COOC}_2\text{H}_5$ , m.p.  $101^\circ$ , is obtained by the condensation of acetosalicylic chloride and sodio malonic ester, sodium chloride and ethyl acetate being set free.  **$\beta$ -Hydroxy- $\alpha$ -cyanocoumarin**, m.p.  $242^\circ$ , and  **$\beta$ -hydroxy- $\alpha$ -acetyl-coumarin**, m.p.  $134^\circ$ , are obtained in a similar manner from acetosalicylic chloride and sodium cyanoacetic or acetoacetic esters (*Anschutz*, Ann. 367, 169). The latter compound seems to be formed also when sodium acts on warm phenyl acetate (*Perkin*, J. 119, 1284).

### 20. Phenylene-hydroxy-olefine Dicarboxylic Acids

Phthalyl acetic acid and isocoumarin-carboxylic acid are related to each other in the same way as methylene-phthalide is to isocoumarin. Phthalyl-acetic acid and its homologues have been prepared from phthalic anhydride by Perkin's reaction.

**Phthalyl-acetic acid**,  $\text{C}_6\text{H}_4\text{C}(\text{COOH})\text{:C}(\text{COO})$ , melts above  $260^\circ$  (decomp.).

When distilled in a good vacuum it decomposes into carbon dioxide and methylene phthalide (p. 482). With excess alkali it gives *o*-carboxy-benzoyl-acetic acid (p. 440). With water, carbon dioxide is given off and *o*-acetyl-benzoic acid is formed. When it is heated with ammonia, *phthalimidacetic acid* is formed, and alkylamines react in a similar manner. It is converted into the sodium salt of the isomeric diketo-hydrindene-carboxylic acid by sodium methylate (*Gabriel*, Ber. 26, 935).

**Isocoumarin-3-carboxylic acid**,  $\text{C}_6\text{H}_4\text{C}(\text{COOH})\text{:C}(\text{COO})$ , m.p.  $227^\circ$ , is obtained from *o*-carboxyphenyl-glycerolic lactone (p. 440) by the action of hydrogen chloride at  $160^\circ$ ; cf. isocoumarin. It is readily converted by ammonia into **isocarbostyryl-3-carboxylic acid**,  $\text{C}_6\text{H}_4\text{C}(\text{COOH})\text{:C}(\text{COO})$ , m.p.  $320^\circ$  (*Bamber-*

ger, Ber. 25, 1138). For the synthesis of the latter from hippuric acid and the ethyl ester of phthalaldehydic acid by way of the oxazolone, see *Bain*, J. 105, 2392. Isocoumarin-carboxylic acid splits into *o*-toluic acid and oxalic acid when boiled with caustic soda (*Bamberger*, Ann. 288, 134). For the formation of  $\gamma$ -hydroxy-isocarbostyryl-carboxylic ester from phthalyl-glycocollic ester, see p. 387.

**Ethyl hydroxy-methylene-homophthalate**,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{C}(\text{:CHOH}) \cdot \text{COOC}_2\text{H}_5 \\ \text{COOC}_2\text{H}_5 \end{array}$ , is a colourless, strongly acidic oil, which is obtained by condensing homophthalic and formic esters. At  $100^\circ$  it is converted into **ethyl isocoumarin-4-carboxylate**,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{C}(\text{COOC}_2\text{H}_5) \cdot \text{CH} \\ \text{CO} \text{---} \text{O} \end{array}$ , m.p.  $68^\circ$ , which is reconverted by alkali into formic and homophthalic acid, and gives **ethyl isocarbostyryl-4-carboxylate**,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{C}(\text{COOC}_2\text{H}_5) \cdot \text{CH} \\ \text{CO} \text{---} \text{NH} \end{array}$ , m.p.  $227^\circ$ , with ammonia.

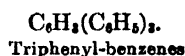
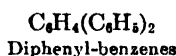
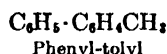
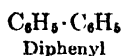
### 21. Phenylene-hydroxy-olefine Tricarboxylic Acid

**Phthalyl-malonic ester**,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{C} \cdot \text{C}(\text{COOC}_2\text{H}_5)_2 \\ \text{CO} \cdot \text{O} \end{array}$ , or  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}(\text{COOC}_2\text{H}_5)_2$  (*Scheiber*, Ann. 389, 121), m.p.  $74^\circ$ , is obtained together with ethyl phthalyl-dimalonate (p. 441) by the action of phthalyl chloride on ethyl sodio-malonate (*Wislicenus*, Ann. 242, 46). **Ethyl phthalyl-cyanoacetate**,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{C} \cdot \text{C}(\text{CN})\text{COOC}_2\text{H}_5 \\ \text{CO} \cdot \text{O} \end{array}$ , m.p.  $175^\circ$ , is obtained from phthalyl chloride and ethyl sodio-cyanoacetate (*Muller*, C.r. 116, 760).

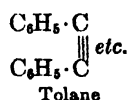
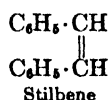
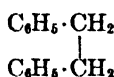
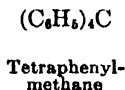
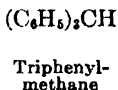
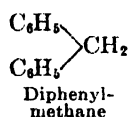
## II. MULTINUCLEAR AROMATIC COMPOUNDS

By A. BUTENANDT and R. TSCHESCHE

In the same way as alkyl groups can be combined with each other, or can be introduced into the benzene nucleus, the hydrogen atoms of the benzene ring can be replaced by phenyl, tolyl, and benzyl groups, and by other hydrocarbon radicals. In this way there are produced: (A) the phenyl-benzenes, in which the benzene nuclei are directly linked with each other, *e.g.*



and (B) the polyphenyl paraffins, olefines, and acetylenes, in which the benzene nuclei are linked together by paraffin residues, *e.g.*,

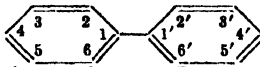


In addition there are (C) the aromatic hydrocarbons with condensed nuclei.

### A. Phenyl-benzene Group

#### 1. DIPHENYL GROUP

The fundamental hydrocarbon of this group is diphenyl, or phenyl-benzene.

Diphenyl, *phenyl-benzene*,  $\text{C}_{12}\text{H}_{10}$ ,  m.p.  $71^\circ$ , b.p.  $254^\circ$ , occurs in small quantities in coal-tar. It is produced (1) by passing benzene through a red-hot tube (*Berthelot*, Z. f. Chem., 1866, 707; *Schultz*, Ber. 9, 547; *La Coste*, Ann. 230, 5); (2) by the action of sodium on bromobenzene in ether or benzene solution, in which case it is accompanied by more highly condensed hydrocarbons (*Fittig*, Ann. 121, 363; *Weiler*, Ber. 29, 115), or better from iodobenzene and copper powder, by heating to  $230^\circ$  (*Ullmann*, Ann. 332, 40); (3) from phenyldiazonium chloride (a) by the action of benzene and aluminium chloride, (b) with benzene and stannous chloride, (c) from phenyldiazonium sulphate by the action of alcohol and copper powder, (d) from phenyldiazonium sulphate by warming with benzene (*Gattermann*, Ber. 23, 1226; *Mohlau*, Ber. 26, 1997); (4) as a by-product in the preparation of phenyl-magnesium halides by the action of phenyl halides on magnesium in ether solution; and

directly from phenyl-magnesium halides by the action of cupric salts or ferric chloride in ether (*Krizewsky*, J. 115, 559; *Michailenko*, C. 1923, III, 1014).

It is oxidised by chromic acid in glacial acetic acid to benzoic acid, and reduced by sodium and amyl alcohol to tetrahydrodiphenyl,  $C_{12}H_{14}$ , b.p.  $245^\circ$ , the dibromide of which is converted into dihydrodiphenyl,  $C_{12}H_{12}$ , b.p.  $248^\circ$ , by the action of alcoholic potash (*Bamberger*, Ber. 21, 846); a dihydrodiphenyl, m.p.  $66^\circ$ , is obtained from the phenyl-dihydroresorcinol (Vol. II, p. 112) of which the tautomeric diketo-form is reduced to the corresponding dihydric cyclohexanol: two molecules of water are removed from this by phosphorus pentoxide (*Knoevenagel*, Ann. 289, 168). Hexahydrodiphenyl, phenyl-cyclohexane,  $C_6H_5 \cdot C_6H_{11}$ , m.p.  $7^\circ$ , b.p.  $239^\circ$ , is obtained by synthesis from benzene and chlorocyclohexane by means of aluminium chloride (*Kurssanov*, C. 1907, I, 1745). Perhydrodiphenyl, dicyclohexyl,  $C_6H_{11} \cdot C_6H_{11}$ , see Vol. II, p. 152.

On treatment with methylene chloride and aluminium chloride, diphenyl gives fluorene (*Adam*, C.r. 103, 207).

ALKYLATED DIPHENYLS can be obtained: 1. from their amino-compounds by the action of nitrous acid in alcoholic solution (*Schultz*, Ber. 17, 468; *Stolle*, Ber. 21, 1096); 2. from bromo-alkylbenzenes by the action of sodium; compounds belonging to the diphenylmethane and dibenzyl series are obtained as by-products in these reactions (*Zincke*, Ber. 4, 396; *Weiler*, Ber. 32, 1056; 33, 334); 3. from iodo-alkyl-benzenes by heating with copper powder (*Ullmann*, Ann. 332, 38; *Schreiner*, J. pr. [2], 81, 422); 4. from diphenyl, alkyl or ethylene chloride and aluminium chloride (*Adam*, C.r. 104, 691); 5. from aromatic diazonium chlorides, see p. 125. 6. Unsymmetrical diphenyls can be obtained from phenylcyclohexane derivatives, see *Kenner*, J. 1931, 769. The position of the alkyl radical can be determined by oxidation, if it is not obvious from the constitution of the starting material.

*o*-Phenyl-toluene, 2-methyl-diphenyl, b.p.  $255-258^\circ$  (*Kliegl*, Ber. 53, 1655).

*m*-Phenyl-toluene, 3-methyl-diphenyl, b.p.  $272-277^\circ$  (*Adam*, Bull. [2], 49, 98; *Poinier*, *ibid.* [3] 7, 181; *Jacobsen*, Ber. 28, 2546).

*p*-Phenyl-toluene, 4-methyl-diphenyl, m.p.  $49-50^\circ$ , b.p.  $263-267^\circ$  (*Mohlau*, Ber. 26, 1996; *Gomberg*, Ann. 48, 1372).

*m*-Ethyl-diphenyl, 3-ethyl-diphenyl, b.p.  $283^\circ$  (*Adam*, Bull. [2], 47, 689; 49, 101; Ann. chim. [6], 15, 249).

*o,o'*-Ditolyl, 2,2'-dimethyl-diphenyl, m.p.  $17.8^\circ$ , b.p.  $258^\circ$  (*Ullmann*, Ann. 332, 42; *Jacobson*, Ber. 28, 2555).

*m,m'*-Ditolyl, 3,3'-dimethyl-diphenyl, m.p.  $5-7^\circ$ , b.p.  $286^\circ$  (*Perrier*, Bull. [3], 7, 182; *Ullmann*, Ann. 332, 43; *Schultz*, Ann. 352, 112).

*o,m'*-Ditolyl, 2,3'-dimethyl-diphenyl, b.p.  $270^\circ$  (*Schultz*, Ber. 17, 471).

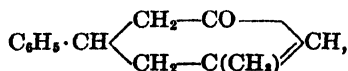
*o,p'*-Ditolyl, 2,4'-dimethyl-diphenyl, b.p.  $272-280^\circ$  (*Carnelley*, J. 29, 13; 32, 653; 37, 707).

*p,p'*-Ditolyl, 4,4'-dimethyl-diphenyl, m.p.  $122^\circ$ , b.p.  $295^\circ$  (*Ullmann*, Ann. 332, 44).

Dimesityl, 2,4,6,2',4',6'-hexamethyl-diphenyl, m.p.  $100^\circ$  (*Meyer*, Am. 51, 630).

For further homologues of diphenyl, see *Gomberg*, Am. 48, 1372; *Moyer*, Am. 51, 630; *Boesker*, Bull. [4], 45, 645.

Hydrated derivatives of the diphenyl series have been obtained by the synthetic methods described on p. 114 of Vol. II for the preparation of cyclohexenone. Thus, phenyl-methyl-cyclohexenone,



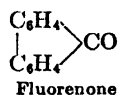
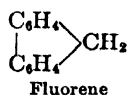
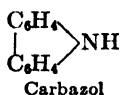
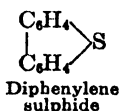
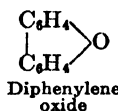
m.p.  $36^\circ$ , is obtained from benzylidene-bis-acetoacetic ester. It gives, on reduction, phenyl-methyl-cyclohexanol,  $C_6H_5 \cdot C_6H_9 \cdot (CH_3) \cdot (OH)$ , b.p.  $177^\circ$  (20 mm.), which is converted into phenyl-methyl-cyclohexene,  $C_6H_5 \cdot C_6H_8 \cdot (CH_3)$ , b.p.  $129^\circ$  (17 mm.), by elimination of water (*Knorr*, Ann. 303, 259); see also phenyl-dihydro-resorcinol. Cyclohexyl-2-cyclohexanol,  $C_6H_{11} \cdot C_6H_{10} \cdot OH$ , m.p.  $31^\circ$ , b.p.  $270^\circ$  is obtained by reduction of cyclohexylidene-cyclohexanone (Vol. II, p. 152) (*Wallach*, Ber. 40, 70).

### Substitution Products of Diphenyl\*

Theory predicts the existence of three isomerides of each mono-substitution product of diphenyl. Cl, Br, NO<sub>2</sub>, SO<sub>3</sub>H, preferentially enter the *p*-position with respect to the linkage between the two benzene nuclei. In addition to the *p*-, and *p,p'*-derivatives, *o,o'*- and *o,p'*-derivatives are also produced. The *p,p'*-derivatives with two different substituents give two different substituted benzoic acids on oxidation. Thus, *p*-bromo-*p'*-nitrodiphenyl give both *p*-bromo- and *p*-nitrobenzoic acids on oxidation (see benzidine). From the aminodiphenyls, and especially from benzidine, or *p,p'*-diaminodiphenyl, and from the diphenyl sulphonic acids, numerous derivatives of diphenyl can be prepared by essentially the same methods as for the corresponding benzene derivatives.

It is noteworthy that *o,o'*-disubstitution products are known in which a divalent atom, such as O and S, or a divalent group, such as NH, CH<sub>2</sub>, CO, replaces two hydrogen atoms in the *o*-position to the link joining the two benzene nuclei.

Of the more important of such diphenylene compounds:



the first three are dealt with as heterocyclic compounds in connection with furan, thiophene, and pyrrole, from which they can also be derived. They are produced by pyrolysis from phenyl ether, phenyl sulphide, and diphenylamine, respectively.

### Optically Active Diphenyl Derivatives. Molecular Asymmetry

A very remarkable type of isomerism is observed in the case of the ortho- (2,6,2',6') substituted diphenyl derivatives. *Kenner* and *Christie* (1922) found that *o,o'*-dinitro-diphenic acid (p. 506) could be resolved into optical antipodes. These mirror-image isomerides were also found for many of the ortho-substituted diphenyl-derivatives investigated. To explain this "molecular asymmetry" it was assumed that in the case of suitable ortho-substituents the rotation of the phenyl nuclei about their axis was limited, the two rings lying in different planes, which could be perpendicular to each other. Compounds of which the isomerism depends on the limitation of free rotation about a simple C—C linkage are called *atropic isomerides* (*Kuhn*). The most important factors affecting the inhibition of free rotation is the space occupied by the substituents in the ortho-positions (*W. H. Mills*); in agreement with this assumption is the fact that atropic isomerism of the diphenyl derivatives is only observed if the calculated volume of the *o*-substituents present is sufficient to prevent a coplanar arrangement of the two benzene rings. Racemisation of the optically active diphenyl derivatives only occurs if the two *o*-substituents can swing over each other. It occurs most readily when not all of the four ortho-positions are occupied. The velocity of racemisation may be regarded as a measure of the hindrance to free rotation. Substitution in the 4,4'-position has no effect on the asymmetry, while substituents in the 3,5,3',5'-positions can contribute to the asymmetry if the *o*-positions are occupied with the same substituents (e. g., 2,2',4,4',6,6'-hexamethyl-3,3'-diaminodiphenyl; *Adams*) (*Meisenheimer*, Ber. 60, 1425; *Mascarelli*, Gazz. 58, 791, 865; *Kuhn*, Ann. 455, 272; *Chalmers*, J. Proc. Roy. Soc. N. S. W.

\* The radical of diphenyl (= diphenyl) is also known as xenyl.



64, 320; *Corbellini*, Atti. R. Accad. Lincei [6], 15, 968; *Shaw*, J. 1933, 135). For a review of the stereochemistry of the diphenyls, see *Adams*, Chem. Rev. 12, 261.

**HALOGENATED DIPHENYLS.** 2- and 4-Chlorodiphenyl, m.p. 32°, b.p. 273.8° and m.p. 77°, b.p. 291°, resp. 2- and 4-Bromodiphenyl, liquid, b.p. 297°, and m.p. 89°, b.p. 310°, resp. 4-Iododiphenyl, m.p. 111°. 4,4'-Difluoro-, 4,4'-dichloro-, 4,4'-dibromo-, and 4,4'-diiododiphenyl, m.p. 87°, 148°, 164°, and 202°, resp. (*Schmidt*, Ann. 207, 333; *Castellane*, Ber. 30, 2800). 2,2'-Dichlorodiphenyl, m.p. 59°. 3,3'-Dichlorodiphenyl, b.p. 320-326° (*Mascarelli*, Gazz. 59, 867). 2,2'-Diiododiphenyl, m.p. 108°, gives with chlorine diphenyl-diiodo-tetrachloride,  $\text{Cl}_2\text{IC}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{ICl}_2$ , m.p. 130-135°, from which 2,2'-diiodoso- and 2,2'-diiodo-diphenyl can be obtained. By the action of potassium

iodide the latter gives diphenylene-iodonium iodide,  $\begin{matrix} \text{C}_6\text{H}_4 \\ \diagup \\ \text{C}_6\text{H}_4 \end{matrix} \text{I}^+\text{I}^-$ , m.p. 211°,

which is also produced, together with 2,2'-diiododiphenyl from the bisdiazonium compound of 2,2'-diaminodiphenyl, and isomerises to the other form of 2,2'-diiododiphenyl on warming (*Mascarelli*, Gazz. 59, 867). For derivatives of 4,4'-diiododiphenyl with polyvalent iodine, see *Willgerodt*, Ber. 42, 3826. For fluorodiphenyls see *Schiemann*, Ber. 62, 1805; 64, 1332.

Perchlorodiphenyl,  $\text{C}_{12}\text{Cl}_{10}$ , does not melt below 270°. It is often obtained in perchlorination reactions (*Merk*, Ber. 16, 2881).

**NITRODIPHENYLS.** Nitration of diphenyl gives *o*- and *p*-nitro, and *o,o'*-, and *o,p'*-dinitrodiphenyl. Symmetrical di- and poly-nitrodiphenyls are easily obtained from *o*- and *p*-halogeno-nitrobenzenes, and from *m*-iodonitrobenzenes by heating with copper powder (*Ullmann*, Ber. 34, 2174); they are also obtained by the decomposition of the diazonium salts of the nitranilines with hydrochloric acid or ammoniacal cuprous oxide solution (*Ullmann*, Ber. 34, 3802; 38, 725; *Vorländer*, Ann. 320, 123). *o,o'*- and *m,m'*-Dinitrodiphenyl can also be obtained from benzidine (*Brunner*, Ber. 20, 1028).

*o*-(2)-Nitrodiphenyl, m.p. 37°, b.p. 320° (*Liddens*, Ber. 8, 871; *Hübner*, Ann. 209, 341).

*m*-(3)-Nitrodiphenyl, m.p. 61° (*Jacobson*, Ber. 36, 4083; *Fichter*, Ber. 37, 882).

*p*-(4)-Nitrodiphenyl, m.p. 114°, b.p. 340° (*Kühling*, Ber. 28, 42; *Schultz*, Ann. 174, 210; *Hübner*, Ann. 209, 340).

*o,o'*-(2,2')-Dinitrodiphenyl, m.p. 125° (*Ullmann*, Ber. 34, 2176; 38, 725).

*m,m'*-(3,3')-Dinitrodiphenyl, m.p. 200° (*Ullmann*, Ber. 34, 2177; 38, 726).

*p,p'*-(4,4')-Dinitrodiphenyl, m.p. 235° (*Ullmann*, Ber. 34, 2177; *Willstätter*, Ber. 39, 3478; *Fittig*, Ann. 124, 276; *Meyer*, Ann. 320, 134).

*o,p*-(2,4')-Dinitrodiphenyl, m.p. 93° (*Kühling*, Ber. 29, 166).

These dinitrodiphenyls are obtained, amongst other products, from nitrobenzene and sodium nitrophenyl-*anti*-diazotate.

2,2',4,4'-Tetranitrodiphenyl is obtained from 1,2,4-chloro(bromo)-dinitrobenzene and copper powder; m.p. 165-166° (*Ullmann*, Ber. 34, 2177; Ger. Pat. 129,147).

3,3',4,4'-Tetranitrodiphenyl is obtained from 1,3,4-iododinitrobenzene and copper powder, m.p. 186° (*Ullmann*, Ber. 34, 2179).

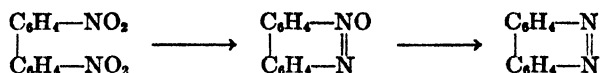
2,2',4,4',6,6'-Hexanitrodiphenyl, m.p. 238°, is obtained from picryl chloride (p. 63) and copper powder (*Ullmann*, loc. cit.).

4-Bromo-4'-nitrodiphenyl, m.p. 173°, see *Schultz*, Ann. 174, 218.

4,4'-Dichloro-2,2'-dinitrodiphenyl, m.p. 136°, is obtained from 2,5-dichloronitrobenzene or 4,2-chloro-nitraniline (*Ullmann*, Ber. 34, 3803).

For other halogeno- and hydroxy-nitrodiphenyls, see *Borsche*, Ber. 50, 596; *Raudnitz*, Ber. 60, 738; *Blakey*, J. 1927, 3000; *Hinkel*, J. 1929, 1838; *Gull*, J. 1929, 491.

When the 2,2'-dinitrodiphenyls are reduced by sodium amalgam in alcohol, sodium sulphide, stannous chloride and hydrochloric acid, or electrolytically, cyclic azoxy-compounds are first produced called phenazone oxides, and then azo-compounds, called phenazones (*Ullmann*, Ber. 37, 23). These compounds will be dealt with more fully under the *ortho*-diazines:



**AMINODIPHENYLS** and **AMINODITOLYLS** can be prepared by the reduction of the corresponding nitro-compounds. Of outstanding technical importance is the formation of 4,4'-diaminodiphenyl by the transformation of hydrazobenzene (p. 143) with which it is isomeric, since 4,4'-diaminodiphenyl or benzidine is the starting material for the preparation of substantive cotton dyes, *i.e.*, dyes which attach themselves directly to the fabric without the use of mordants.

*o*-(2)-Aminodiphenyl, m.p. 49°, is produced from *o*-phenyl-benzamide by the action of bromine and caustic alkali (Graebe, Ann. 279, 286; Hirsch, Ber. 25, 1974). On passing over heated lime it is converted into carbazole. *m*-(3)-Aminodiphenyl, m.p. 30° (Fichter, Ber. 37, 882). *p*-(4)-Aminodiphenyl, xenylamine, m.p. 54°, b.p. 322° (Heusler, Ann. 260, 233; Pummerer, Ber. 54, 2768; reaction of benzene with azobenzene hydrochloride in the presence of aluminium chloride, *cf.* *p*-amino-terphenyl). *p,p'*-(4,4')-Nitroaminodiphenyl, m.p. 198°, is obtained from *p,p'*-(4,4')-dinitrodiphenyl.

*o,o'*-(2,2')Diaminodiphenyl, m.p. 81°, and *m,m'*-(3,3')diaminodiphenyl are obtained by the reduction of *o,o'*- and *m,m'*-dinitrodiphenyl, respectively. If *o,o'*-(2,2')diaminodiphenyl is heated with concentrated sulphuric acid it is converted into carbazole. Its *bis*-diazonium chloride gives carbazole with potassium hydrosulphide, and on warming the aqueous solution diphenylene oxide is formed (Täuber, Ber. 26, 1703). By reduction of the *bis*-diazonium compound of *o,o'*-(2,2')-diaminodiphenyl, diphenylene-*o,o'*-(2,2')-dihydrazine,

$\begin{array}{c} \text{C}_6\text{H}_4[2]\text{NHNH}_2 \\ | \\ \text{C}_6\text{H}_4[2']\text{NHNH}_2 \end{array}$ 
, m.p. 110°, is obtained (Täuber, Ber. 29, 2270). On heating

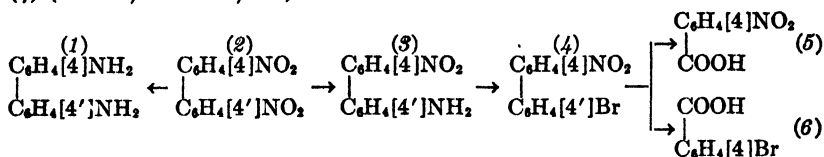
with hydrochloric acid to 150°, this is broken down into ammonium chloride and phenazone (see above).

**Benzidine**, 4,4'-diaminodiphenyl, m.p. 127° (Zinin, 1845), is produced by reduction of 4,4'-dinitro- and 4,4'-nitroamino-diphenyl. It is prepared technically by the reduction of azobenzene in acid solution, the hydrazobenzene first formed being further converted into benzidine and *o,p'*-diaminodiphenyl (diphenylene), a reaction which has already been discussed in connection with hydrazobenzene (p. 145) (Schmidt, Ann. 207, 330).

The benzidine is separated from the diphenylene by making use of the sulphate of the former, which is almost insoluble in water. Treatment with concentrated sulphuric and nitric acids results in the introduction of one or two NO<sub>2</sub>-groups in the *m*-position to the amino-groups of benzidine. Nitro-*p,p'*-diaminodiphenyl, and *o,o'*-dinitro-*p,p'*-diaminodiphenyl (Täuber, Ber. 23, 794) are produced. If diacetbenzidine is nitrated, *m,m'*-dinitro-*p,p'*-diacetamino-diphenyl is formed. By the action of chlorine and bromine, the four hydrogen atoms in the *o*-position to the amino-groups are substituted (Schlenk, Ann. 363, 332). Oxidation with lead dioxide in indifferent solvents converts benzidine into *p,p'*-diaminoazodiphenyl (p. 499), with the intermediate formation of the unstable *p,p'*-diphenoquinone-diimine (p. 503) (*cf.* the analogous conversion of *o*-phenylene diamine into *o,o'*-diaminoazobenzene, p. 142) (Willstätter, Ber. 39, 3474). On the other hand, benzidine is oxidised by permanganate, ferric chloride, potassium ferricyanide, chromic acid, *etc.*, in acid solution, to a blue dye ("benzidine blue"), which apparently belongs to the class of quinhydrones and is analogous in structure to Wurster's dyes (p. 243) (Schlenk, Ann. 363, 324; Willstätter, Ber. 41, 3248).

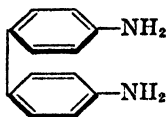
**Constitution.**—The *p*-position of the two amino-groups in benzidine (1) follows

from the oxidation of 4,4'-bromonitrodiphenyl to *p*-bromo- and *p*-nitrobenzoic acids (5,6), since benzidine (1) is formed from 4,4'-dinitrodiphenyl (2), which can be converted into 4,4'-aminonitrodiphenyl (3), and 4,4'-bromonitrodiphenyl (4) (Schultz, Ann. 174, 227).



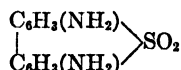
The constitution of benzidine is the basis of one proof of the constitution of diphenic acid (p. 505), and thus of that of phenanthrene, isomeric with anthracene.

Benzidine has a linear molecular structure. *Kauffer* proposed a formula for benzidine in which the two benzene nuclei did not lie in one plane, but were arranged over each other in space:



This formula was, however, based on erroneous observations (Ann. 357, 151; Ber. 40, 3250). The linear formula, in which the two amino groups lie in the same straight line as the nuclei, has been confirmed by the determination of the first and second dissociation constants of benzidine. This agrees with the value to be expected for the linear molecule (*Kuhn*). The non-polar character of the 4,4'-substituted diphenyls is undoubted proof of the linear molecular form (*Kuhn*, Ann. 455, 254; *Turner*, J. 1926, 2476).

**Benzidine sulphate** forms small scales with a silvery lustre. For preparation, see *Teichmann*, Z. angew. Ch. 1893, 67. On heating with concentrated sulphuric acid it gives benzidine sulphone:



(*Griess*, Ber. 22, 2467). **Diacetobenzidine**, m.p. 317°. Thionyl-benzidine,  $(\text{C}_6\text{H}_4 \cdot \text{N} : \text{SO})_2$  (*Michaelis*, Ber. 24, 753). Di-(*o*-nitrobenzyl)-benzidine, m.p. 227° (decomp.) (*Francis*, Ber. 29, 1450).

2,6,2',6'-Tetrachloro- and tetrabromo-benzidines, m.p. 227° and 288°, respectively, see above.

**N,N'-Dimethylbenzidine**,  $\text{CH}_3\text{NHC}_6\text{H}_4 \cdot \text{C}_6\text{H}_4\text{NHCH}_3$ , m.p. 81–82°, see *Kuhn*, Ber. 37, 3771; reaction with oxidising agents, see *Willstätter*, Ber. 41, 3250.

**N,N'-Tetramethylbenzidine**,  $(\text{CH}_3)_2\text{NC}_6\text{H}_4 \cdot \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ , m.p. 197°, is also obtained from dimethylaniline by oxidation with concentrated sulphuric acid at 190–200°, or by electrochemical oxidation at a lead dioxide anode (*Ullmann*, Ber. 37, 29; *Fichter*, Helv. 5, 166). **N,N'-Diphenylbenzidine**,  $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4 \cdot \text{C}_6\text{H}_5\text{NHC}_6\text{H}_5$ , m.p. 242° is formed by the action of fuming sulphuric acid on diphenylamine (*Kadiera*, Ber. 38, 3575).

**2-Nitro-4,4'-diaminodiphenyl**, *m*-nitrobenzidine, m.p. 143° (*Täuber*, Ber. 23, 796), see benzidine. **2,2'-Dinitro-4,4'-diaminodiphenyl**, *m*-dinitrobenzidine, m.p. 214° (*Täuber*, loc. cit.). **3,3'-Dinitro-4,4'-diaminodiphenyl**, *o*-dinitro-benzidine, m.p. 275° (*Cain*, J. 101, 2298; 103, 586). **2,3'-Dinitro-4,4'-diaminodiphenyl**, m.p. 236° (*Turner*, J. 1926, 1759). **2,2'-Dinitro-tetramethyl- and -tetraethylbenzidine** form red needles, m.p. 229° and 132°, resp. (*Ullmann*, Ber. 37, 29, 34). **3,3'-Dinitro-4,4'-diacetodiamino-diphenyl** melts above 300°. **5,5'-Dinitro-2,2'-diaminodiphenyl** (*Täuber*, Ber. 25, 128).

**2,4'-Diaminodiphenyl**, diphenylene, m.p. 45°, b.p. 362°; preparation, see benzidine (*Schultz*, Ann. 207, 348; *Reuland*, Ber. 22, 3011). **2,4,4'-Triamino-diphenyl**, *m*-aminobenzidine, see *Täuber*, Ber. 23, 797. **2,4,2',4'-Tetramino-**

diphenyl, *m,m'*-diaminobenzidine, m.p. 165°, is prepared from 2,2'-dinitro-4,4'-diaminodiphenyl (see benzidine), or from *m,m'*-diamino-hydrazobenzene (*Elbs*, J. pr. 2, 66, 561), and is converted into *p,p'*-diaminocarbazole by elimination of ammonia.

*Di-p-phenylene diamine*,  $(\text{NH}_2)_2[2,5]\text{C}_6\text{H}_3\cdot\text{C}_6\text{H}_3[2',5'](\text{NH}_2)_2$ , m.p. 168°, is converted by heating with hydrochloric acid to 180° into 5,5'-diaminocarbazole (*Täuber*, Ber. 25, 131).

*Diaminodixenylamine*,  $\text{NH}(\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ , m.p. 221°, is obtained by heating benzidine with benzidine hydrochloride (*Merz*, J. pr. [2] 61, 103).

**HOMOLOGOUS BENZIDINES.** 3-Methyl-4,4'-diaminodiphenyl, *o*-methyl benzidine,  $\text{NH}_2\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_3(\text{CH}_3)\text{NH}_2$ , m.p. 90°, was obtained from nitrobenzene and *o*-nitrotoluene (*Hirsch*, Ber. 23, 3222).

3,3'-Dimethyl-4,4'-diaminodiphenyl, *o*-tolidine, m.p. 128°, is obtained from *o*-hydrazotoluene (*Guilermann*, Ber. 20, 2017; *Noelting*, Ber. 23, 3253; *Schultz*, Ann. 352, 111).

An interesting example of steric hindrance is afforded by the action of cyanogen bromide and iodo-acetonitrile on the *N,N'*-tetramethyl derivatives of these two homologous benzidines. While *N,N'*-tetramethyl-3-methyl-benzidine (b.p. 225°) is easily attacked by these reagents, *N,N'*-tetramethyl-3,3'-dimethyl-benzidine (m.p. 78°) is hardly attacked at all under the same conditions (*von Braun*, Ber. 50, 1651).

2,2'-Dimethyl-4,4'-diaminodiphenyl, *m*-tolidine, m.p. 109°, is obtained from *m*-hydrazotoluene (p. 144). Ditolyline, isomeric with this compound, is obtained at the same time (*Noelting*, Ber. 23, 3252).

While *o*- and *m*-hydrazotoluene undergo the benzidine transformation with acids, *p*-hydrazotoluene undergoes the semidine transformation under these conditions.

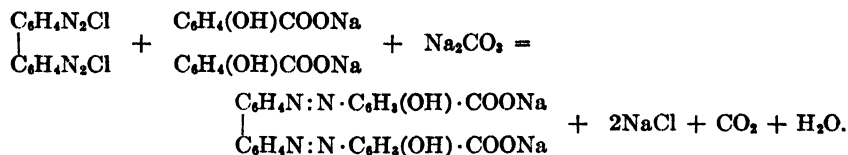
3,3'-Diethyl-4,4'-diaminodiphenyl is obtained from *o*-nitro-ethylbenzene (*Schultz*, J. pr. [2], 66, 153).

**Diazoamino- and azo-compounds of diphenyl.** Diphenyl-*bis*-diazonium chloride, obtained by diazotisation of benzidine in hydrochloric acid solution combines with 2 mols. of aniline to give

Diphenyl-*bis*-diazoaminobenzene,  $\text{C}_6\text{H}_5\text{NH}\cdot\text{N}:\text{NC}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{N}:\text{N}\cdot\text{NHC}_6\text{H}_5$ , forming yellow-red crystals, m.p. 180°, which can also be obtained from benzidine and phenyldiazonium chloride. On heating with aniline and aniline hydrochloride it isomerises to diphenyl-*bis*-azoaminobenzene,  $\text{NH}_2\text{C}_6\text{H}_4\text{N}:\text{NC}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{N}:\text{NC}_6\text{H}_4\text{NH}_2$ , m.p. 159° (*Vignon*, C.r. 142, 582).

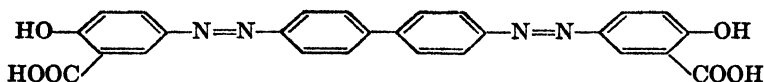
*p,p'*-Diaminoazodiphenyl,  $\text{NH}_2[4]\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{N}:\text{NC}_6\text{H}_4\cdot\text{C}_6\text{H}_4[4']\text{NH}_2$ , m.p. 287°, is produced by the oxidation of benzidine with lead dioxide (p. 497), as well as by the reduction of *p,p'*-aminonitrodiphenyl with zinc dust and sodium hydroxide, and oxidation of the hydrazo-compound thus obtained (*Willstätter*, Ber. 39, 3479).

**BENZIDINE AZO DYES.** The reaction products of the diazonium chloride of benzidine with amino-sulphonic acids, phenol-carboxylic acids, and phenol-sulphonic acids are of outstanding technical importance, since they dye cotton directly (*Griess*, Ber. 22, 2469). The dyestuff concerned is prepared in the form of its sodium salt, the aqueous solution of the *bis*-diazonium chloride being poured into the aqueous solution of two mols. of the sodium salt of the other component, the hydrochloric acid set free being neutralised by the addition of sodium carbonate; sodium acetate, or ammonia:



Diphenyl-*bis*-diazonium chloride can be conveniently prepared in the solid state, and one of its diazo-groups is more reactive than the other (*cf. Castellana*, Ber. 30, 2800; *Wedekind*, Ber. 31, 482). It is therefore possible to act upon the sodium salt with two different substances in stages, and thus prepare mixed *bis*-diazo-dyes (*Lange*, Ber. 19, 1697; *Martius*, *ibid.*, 1755; Ger. Pats. 38,795 and 40,954).

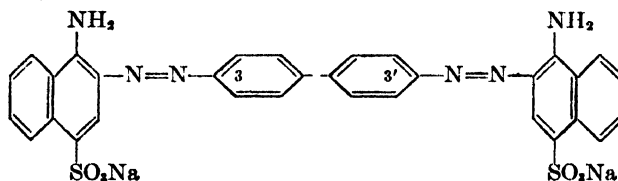
The following may be mentioned as members of the class of benzidine dyes:  
**Chrysamine, flavophenine,**



obtained from diphenyl-*bis*-diazonium chloride and sodium salicylate (equation above).

**Congo yellow,**  $\text{C}_6\text{H}_4 \cdot \text{N} \text{ : } \text{N} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{SO}_2\text{Na}$ , obtained from diphenyl-*bis*-diazonium chloride by the action of phenol and sulphanilic acid. Both are yellow cotton dyes.

The first commercial red dye was Congo red, which was obtained from diphenyl-*bis*-diazonium chloride and sodium naphthionate, and was later classed among the naphthalene azo-dyes:



Materials dyed with Congo red are very sensitive to acid, and are turned blue by mineral acids. Congo red is therefore used as an indicator for the detection of mineral acids. **Benzopurpurin 4B** is derived from Congo red by the introduction of two methyl groups in the 3,3'-positions in the diphenyl nuclei. It is obtained from tolidine and naphthionic acid, and is one of the most important of the red cotton dyes. It is less sensitive to acids than Congo red. The  $\beta$ -naphthylamine sulphonic acids are particularly valuable in preparing substantive cotton dyes.

Similar substantive dyes to those given by benzidine are obtained from 4,4'-aminomethyl-diphenyl, *o*-methyl-benzidine, *o*-, and *m*-tolidine, diamisidine (p. 501), thiobenzidine, thiotolidine (Ger. Pat. 38,795), *p,p'*-diaminobenzophenone (p. 519), and *p,p'*-diaminostilbene (p. 561) (Ger. Pat. 43,204).

In the case of substituted benzidines, nitro- and sulpho-benzidines, and tolidines, it is a *general rule* that those which are substituted in the meta-position to the amino-group give rise to inactive, or very weak substantive azo-dyes. Diamino-diphenylene oxide (Ger. Pat. 51,570), benzidine-sulphone (p. 498) and diamino-carbazole, which contain a third ring, are exceptions (Noelling, Ber. 23, 3252; Hirsch, Ber. 24, 1958).

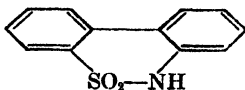
It is noteworthy that benzidine hydrochloride itself combines with cotton and mordants it. It is therefore possible to produce the benzidine dyes actually on the thread (Mohlau, Ber. 19, 2014).

Semi-diazotisation of benzidine is carried out by the action of a diphenyl-*p*-*bis*-diazonium salt on the aqueous solution of a benzidine salt (Täuber, Ber. 27, 2627); cf. the migration of the diazo-group (p. 114). On the action of acetoacetic ester, malonic ester, and cyanoacetic ester on the *bis*-dazo-compounds of benzidine, see Wedekind, Ann. 295, 332; Favrel, C.r. 128, 318; Bull. [3], 27, 104, 313, 324.

4-Hydrazodiphenyl,  $\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_4[4]\text{NH} \cdot \text{NH}_2$  (Müller, Ber. 27, 3105).

4,4'-Dihydrazodiphenyl,  $(\text{C}_6\text{H}_4 \cdot \text{NHNH}_2)_2$ , m.p. 167° (decomp.), gives a characteristic hydrazone with formaldehyde (Neuberg, Ber. 32, 1961); see also diphenylene-*o,o'*-dihydrazine, p. 497.

**DIPHENYL-SULPHONIC ACIDS.** When diphenyl is warmed with sulphuric acid, the first product is diphenyl-4-sulphonic acid, chloride, m.p. 115°, amide, m.p. 229°, and then diphenyl-4,4'-disulphonic acid, m.p. 72°, chloride, m.p. 203° (Gabriel, Ber. 13, 390). If the potassium salt of diphenyl-4-sulphonic acid is heated it is converted into diphenyl and the potassium salt of diphenyl-4,4'-disulphonic acid. Diphenyl-2,2'-disulphonic acid is obtained from benzidine 2,2'-disulphonic acid (Limpricht, Ann. 261, 310).

**Diphenylene-sultam,**

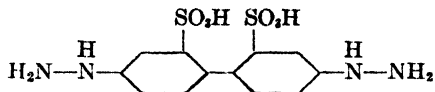
m.p. 196°, forms colourless crystals, strongly acidic in character, and is obtained from the diazonium compound of *o*-aminobenzene-sulphanilide on heating in acid solution (*Ullmann*, Ber. 43, 2694).

For diphenyl-4,4'-dimercaptan, m.p. 175°, obtained from benzidine via the diazonium xanthate, and for its derivatives see *Zincke*, Ber. 45, 3457.

**BENZIDINE SULPHONIC ACIDS:** 4,4'-diamino-diphenyl-3,3'-disulphonic acid is obtained by heating benzidine with sulphuric acid to 210° (*Griess*, Ber. 22, 2466; *Schultz*, Ber. 39, 3341). 4,4'-Diamino-diphenyl-2,2'-disulphonic acid is obtained from *m*-hydrazobenzene sulphonic acid (*Limpricht*, Ann. 261, 310; 268, 130; *Elbs*, J. pr. [2], 66, 558). It gives 4,4'-diamino-diphenylene oxide when fused with caustic potash.

*o*-Tolidine-disulphonic acid, 4,4'-diamino-5,5'-dimethyl-diphenyl-2,2'-disulphonic acid, see *Heller*, Ann. 270, 359.

4,4'-Dihydrazo-diphenyl-2,2'-disulphonic acid (see *Limpricht*, Ann. 261, 323):

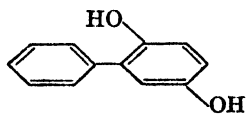


For derivatives of diphenyl with halogen and SO<sub>3</sub>H groups in the same molecule, see *Courtot*, Bull. [4], 49, 1047.

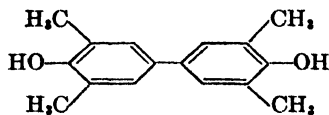
**HYDROXY-DIPHENYLS** are produced from diphenyl derivatives by methods similar to the preparation of phenols from benzene derivatives, and also by oxidation of multinuclear phenols, e.g., by fusion with alkali (*Haussermann*, Ber. 27, 2107).

**MONOHYDROXY-DIPHENYLS.** *p*-Hydroxy-diphenyl, C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>4</sub>[4]OH, m.p. 165°, b.p. 306°, is produced from phenyldiazonium chloride by the action of phenol (*Hirsch*, Ber. 23, 3708).

**DIHYDROXY-DIPHENYLS.** 2,2'-Dihydroxy-diphenyl, m.p. 109°, b.p. 326°, is formed from diphenyl-*o,o'*-disulphonic acid (*Limpricht*, Ann. 261, 332), and from diphenylene oxide (from coal-tar) by fusion with alkali (*Kraemer*, Ber. 34, 1662). On fusion with zinc chloride it is converted into diphenylene oxide. Its dimethyl ether, m.p. 155°, b.p. 308°, is produced by the action of sodium or copper powder on *o*-iodoanisole. An ethylene ether, m.p. 98°, is obtained by the action of ethylene dibromide (*Diels*, Ber. 35, 302). 3,3'-Dihydroxy-diphenyl, m.p. 123.5°, is obtained from *o*-dianisidine and from *m,m'*-diaminodiphenyl (*Haussermann*, Ber. 27, 2107), or by fusion of the disulphonic acid with caustic potash at 250°. (For its nitro-derivatives, particularly hexanitro-3,3'-dihydroxy-diphenyl, dipicric acid, m.p. above 270°, see *Borsche*, Ber. 50, 827.) 4,4'-Dihydroxy-diphenyl, m.p. 275°, is obtained from benzidine, diphenyl-*p,p'*-disulphonic acid, from *p,p'*-diphenylquinone (p. 503) by reduction, and from phenol by the action of permanganate (*Diarin*, Ber. 25, R 335). 2,4'-Dihydroxy-diphenyl, m.p. 160°, is obtained from diphenylene. 2,5-Dihydroxy-diphenyl (see below), m.p. 97°, is obtained by reduction of phenyl-benzoquinone. 3,5,3',5'-Tetramethyl-4,4'-dihydroxy-diphenyl (see below), m.p. 221°, is obtained from tetramethyl-diphenylquinone.



2,5-Dihydroxy-diphenyl



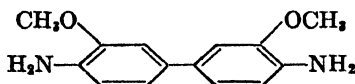
Tetramethyl-dihydroxydiphenyl

**TRIHYDROXY-DIPHENYLS.** 4,3',6'-Trihydroxy-diphenyl, m.p. 234.5°, is obtained from benzoquinone and diazotised *p*-anisidine, with subsequent reduction and demethylation (Kögl, Ann. 482, 105).

**TETRAHYDROXY-DIPHENYLS.** Dicatechol,  $(\text{HO})_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , m.p. 229°, diresorcinol, m.p. 310°, and dihydroquinone, m.p. 237°, are obtained from the three dihydroxy-benzenes by fusion with caustic soda (Barth, Ber. 11, 1336; 12, 503; von Friedrichs, C. 1916, I, 974; Späth, Mo. 55, 342). A resorcylihydroquinone, 2,5,2',5'-tetrahydroxy-diphenyl, m.p. 131°, is obtained by condensation of benzoquinone with resorcinol (Pummerer, Ber. 60, 1442).

**HEXAHYDROXY-DIPHENYLS.** Hexahydroxy-diphenyl,  $(\text{HO})_2\text{C}_6\text{H}_3 \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , is produced by atmospheric oxidation of pyrogallol in baryta solution (Harries, Ber. 35, 2594). An isomeric 3,4,5,3',4',5'-hexahydroxy-diphenyl has been obtained from its 3,4,3',5'-tetramethyl ether, hydrocoerulignon,  $\text{C}_{18}\text{H}_{18}\text{O}_6$ , m.p. 190°, by heating with concentrated hydrochloric acid (Hofmann, Ber. 11, 797; Graebe, Ann. 340, 230). For further derivatives of hexahydroxy-diphenyls, see Liebermann, Ber. 45, 1218.

**AMINO-HYDROXY-DIPHENYLS** are produced from hydroxy-diphenyls (Hirsch, Ber. 22, 335), and from alkyl ethers of hydroxy-azo compounds with the *p*-position free, by the benzidine transformation (Noetting, Ber. 23, 3256). In the coal-tar industry, *o*-dianisidine, or 4,4'-diamino-3,3'-dimethoxy-diphenyl,

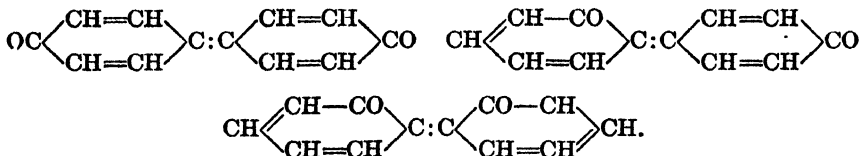


obtained from *o*-nitroanisole, and ethoxybenzidine, are of importance, since their diazonium salts give violet, blue, and black substantive dyes with aminonaphthalene sulphonic acids, naphthol-sulphonic acids, and amino-naphthol-sulphonic acids. Among these dyes are azo-violet, benzazurine, and diamine black (Ger. Pats. 47,136, 53,499, and 53,567).

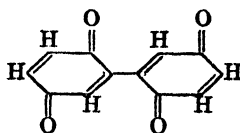
2,5-Amino-hydroxy-diphenyl,  $\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_3[2,5](\text{OH})(\text{NH}_2)$ , m.p. 199°, is obtained by reduction of 2,5-nitroso-hydroxy-diphenyl,  $\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_3[2,5](\text{OH})(\text{NO})$ , which is formed by the action of phenyldiazonium chloride on sodium *p*-nitrosophenate (p. 122). The latter gives 2,5-nitrohydroxy-diphenyl, m.p. 126°, on oxidation, a compound which can also be obtained by the action of benzyl methyl ketone,  $\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_3$ , on nitromalonaldehyde,  $\text{NO}_2\text{CH}(\text{CHO})_2$  (see p. 25) (Hill, Am. Chem. J. 33, 1). 4,4'-Amino-hydroxy-diphenyl, m.p. 271.5°, is obtained from phenylhydroxylamine, phenol, and concentrated sulphuric acid (Bamberger, Ann. 390, 152), and is also produced from phenyldiazonium chloride and phenol by the action of zinc chloride (Pummerer, Ber. 59, 2175).

**QUINONES OF THE DIPHENYL SERIES.** Phenylbenzoquinone,  $\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_4\text{O}_2$ , m.p. 114°, is obtained by the oxidation of 2,5-amino-hydroxy-diphenyl (see above), or of *o*-amino-diphenyl by manganese dioxide and sulphuric acid, and gives with sulphurous acid, a stable quinhydrone, which is also formed by the oxidation of 2,5-dihydroxy-diphenyl (see above) by the air, the latter compound being itself obtained by the action of stronger reducing agents (Borsche, Ann. 312, 211; Fichter, Ber. 37, 878).

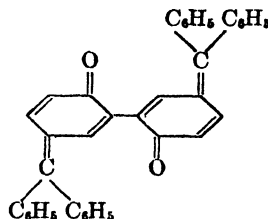
Special interest attaches to a series of quinone compounds of diphenyl in which the two quinone oxygen atoms belong to different benzene rings. The following three fundamental forms of these so-called binuclear quinones are possible. They are referred to as *p,p'*-, *o,p'*- and *o,o'*-diphenoquinone:



Up to the present only *p,p'*-diphenoquinone has been prepared in the free state, but N-containing derivatives (quinone-chlorimines) of the other forms are also known (Schlenk, Ann. 368, 271). In addition, derivatives of a diparaquinone:



e.g., 3,3'-difuchsonyl (*Bistrzycki*, *Helv.* 11, 261) are known:

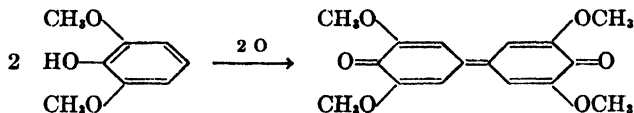


*p,p'*-Diphenoquinone,  $O: C_6H_4: C_6H_4: O$ , decomp. at  $165^\circ$ , is produced by the oxidation of *p,p'*-diphenol with silver oxide or lead dioxide in benzene. It crystallises in two modifications, hard prisms, resembling chromic acid, and soft, fine, needles. With regard to its oxidising action, it resembles *p*-benzoquinone. Reducing agents convert it into *p,p'*-diphenol, **diphenoquinhydrone**, dark-green needles, decomp. at  $180^\circ$ , being formed as an intermediate product (*Willstätter*, *Ber.* 38, 1232).

3,5,3',5'-Tetramethyl-*p,p'*(4,4')-diphenoquinone,  $O: C_6H_2(CH_3)_2: C_6H_2(CH_3)_2: O$ , m.p. about  $210^\circ$ , red needles, is formed on oxidation of *vic-m*-xylenol with chromic acid. It gives tetramethyl-dihydroxy-diphenyl (see p. 501) on reduction. The corresponding quinhydrone, m.p.  $201^\circ$ , forms steel-blue leaflets (*Auwers*, *Ber.* 38, 226).

Tetrachloro- and tetrabromo-*p,p'*-diphenoquinone are obtained by the oxidation of the corresponding diphenol derivatives with fuming nitric acid in glacial acetic acid. They form infusible dark red crystals with a bluish lustre which are reduced to the starting substance by sulphurous acid (*Magatti*, *Ber.* 13, 224).

**Coerulignon** or **cedrilet** is to be considered as a 3,5,3',5'-tetramethoxy-4,4'-diphenoquinone. It separates as a violet powder in the technical purification of pyrolineous acid with potassium dichromate. It is probably formed from dimethyl-pyrogallol, contained in beech-wood tar (p. 229) by oxidation, and can be obtained in this way by the action of potassium chlorate or ferric chloride:



Coerulignon is insoluble in the usual solvents. It is precipitated from its solution in phenol by alcohol or ether, in steel-blue fine needles. It dissolves in concentrated sulphuric acid with a beautiful cornflower-blue colour. On addition of much water the solution returns to its red colour. Reducing agents (tin and hydrochloric acid) convert coerulignon into the colourless hydrocoerulignon (p. 502). The latter, on oxidation, is reconverted into coerulignon. It reacts with primary aromatic amines with the production of blue dyes (*Liebermann*, *Ber.* 30, 235).

For the action of alcoholic hydrogen chloride on coerulignon, see *Liebermann*, *Ber.* 31, 615; cf. also *Schlenk*, *Ann.* 368, 276.

**ALDEHYDES AND KETONES OF THE DIPHENYL SERIES.** *o*-Phenyl-benzaldehyde,  $C_6H_5 \cdot C_6H_4[2]CHO$ , b.p.  $184^\circ$  (21 mm.), is produced by the distillation of *o*-phenyl-benzoic acid with calcium formate. *p*-Phenyl-benzaldehyde, m.p.  $57^\circ$ , b.p.  $184^\circ$  (11 mm.), is obtained from diphenyl-glyoxylic acid,  $C_6H_5 \cdot C_6H_4CO \cdot COOH$ , m.p.  $170^\circ$ , of which the ester is obtained by condensation of diphenyl and ethoxalyl chloride, in the presence of aluminium chloride (*Roussel*, *Bull.* [3], 17, 809; *Fanto*, *Mo.* 19, 584). 4,4'-Diphenyl-dialdehyde,



$\text{CHO}[4]\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4[4']\text{CHO}$ , m.p.  $145^\circ$ . Its dianil is obtained by heating *p*-iodo-benzylidene-aniline with copper powder (Ullmann, Ann. 332, 76). 2,2'-Diphenyl-dialdehyde, m.p.  $67^\circ$ , is obtained from  $\omega,\omega,\omega',\omega'$ -tetrabromo-2,2'-ditolyl, m.p.  $138^\circ$ , and is converted by alkali into  $\omega$ -hydroxy-2-methyl-diphenyl-2'-carboxylic acid,  $\text{HO}\cdot\text{CH}_2[2]\text{C}_6\text{H}_4\text{---C}_6\text{H}_4[2']\text{---COOH}$  (Kenner, J. 99, 2101). With potassium cyanide, it gives phenanthraquinone (Mayer, Ber. 45, 1105). *m*-Phenyl-acetophenone,  $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4[3]\text{COCH}_3$ , m.p.  $121^\circ$ , is obtained from diphenyl, acetyl chloride, and aluminium chloride (Willgerodt, J. pr. [2] 81, 394). Nitrophenyl-benzaldehyde,  $\text{NO}_2\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5\text{CHO}$ , and nitrophenyl-acetophenone,  $\text{NO}_2\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{COCH}_3$ , are produced from nitrophenyl-antidiazotate with benzaldehyde and acetophenone, respectively, in the presence of acetyl chloride (Kühling, Ber. 28, 525). *o,o'*-Diacetyl-diphenyl,  $\text{CH}_3\text{CO}[2]\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4[2']\text{COCH}_3$ , m.p.  $84^\circ$ , see Zincke, Ann. 363, 305.

**DIPHENYL CARBOXYLIC ACIDS** are obtained from derivatives of diphenyl in the same way as benzene-carboxylic acids from benzene derivatives.

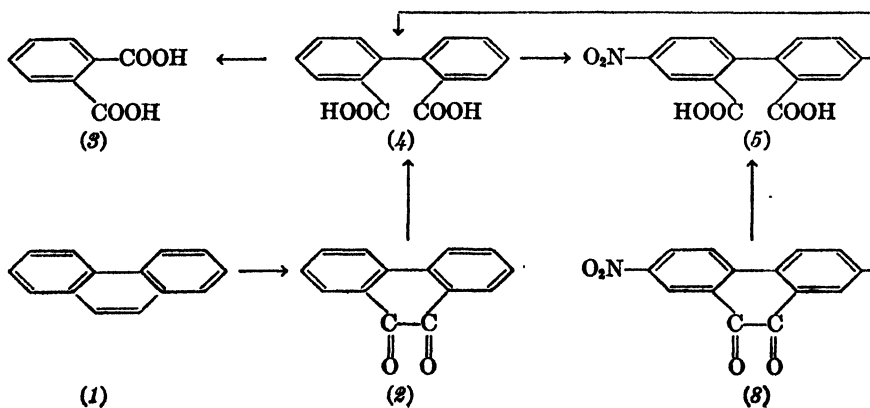
**DIPHENYL MONOCARBOXYLIC ACIDS:** *o*-Phenyl-benzoic acid,  $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4[2]\text{COOH}$ , m.p.  $111^\circ$ , is obtained by fusing diphenylene ketone with caustic alkali (Fittig, Ann. 166, 374), by the distillation of sodium salicylate with triphenyl-phosphate (Richter, J. pr. [2], 28, 305), from *o*-amino- and *o*-methyl-diphenyl. If the acid is treated with phosphorus pentachloride, or heated with sulphuric acid to  $100^\circ$ , or with lime to higher temperatures, it is converted into diphenylene ketone (Pictet, Ann. 266, 142; Graebe, Ann. 279, 259). *o*-(*p*'-Nitrophenyl)benzoic acid, m. p.  $222\text{--}225^\circ$ , obtained by oxidation of *o*-(*p*'-nitrophenyl)-tolyl, yields the corresponding amino acid on reduction (Kühling, Ber. 29, 166). *o*-Phenylcyclohexane-carboxylic acid,  $\text{C}_6\text{H}_5[1]\text{C}_6\text{H}_{10}[2]\text{COOH}$ , m.p.  $150^\circ$ , is obtained synthetically from phenylpentamethylene dibromide and sodio-malonic ester (see Vol. II, p. 19) (Perkin, Jr., Ber. 35, 2122).

*m*-Phenyl-benzoic acid, m.p.  $160^\circ$ , is obtained by oxidation of *m*-methyl-diphenyl, *m*-diphenyl-benzene, and by reduction of bromo-*m*-phenyl-benzoic acid (Olgiati, Ber. 27, 3390). *p*-Phenyl-benzoic acid, m. p.  $218^\circ$ , is obtained from *p*-methyl-diphenyl, *p*-diphenyl-benzene, sodium diphenyl-sulphonate (Rassow, Ann. 282, 143), and *p*-amino-diphenyl, and by fusing benzoic acid with caustic potash. On reduction it is converted into *p*-phenylhexahydro-benzoic acid,  $\text{C}_6\text{H}_5\text{C}_6\text{H}_{10}[4]\text{COOH}$ , which exists in a *cis*- and *trans*-modification, m.p.  $113^\circ$  and  $202^\circ$ , respectively (Rassow, Ann. 282, 139). *p,p'*-Nitrophenyl-benzoic acid, m. p.  $222\text{--}225^\circ$ , is obtained by the oxidation of *p,p'*-nitrophenyl-tolyl, and gives, on reduction, the corresponding amino-acid (Kühling, Ber. 29, 166).

Diphenyl-*m*-acetic acid,  $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4[3]\text{CH}_2\cdot\text{COOH}$ , m.p.  $153^\circ$ , is obtained from *m*-phenyl-acetophenone (see above) by heating with yellow ammonium sulphide (see p. 282).

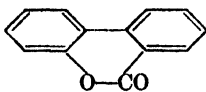
**HYDROXY-DIPHENYL CARBOXYLIC ACIDS.** The following acids are derivatives of *o*-phenyl-benzoic acid:

6-Phenyl-salicylic acid,  $\text{C}_6\text{H}_5[6]\text{C}_6\text{H}_3[2](\text{OH})[1]\text{COOH}$ , m.p.  $159^\circ$ , is formed when 3-hydroxy-diphenylene ketone is fused with alkali (Staedel, Ber. 28, 112).

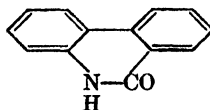


**2-Phenyl-*m*-hydroxybenzoic acid**,  $C_6H_5C_6H_3[6](OH)[2]COOH$ , m.p.  $154^\circ$ , the chief product of fusing 6-hydroxy-diphenylene ketone with alkali (*Graebe*, Ann. 284, 307). At the same time *o*-hydroxyphenyl-*o'*-benzoic acid is formed (p. 505).

***o*-Hydroxyphenyl-*o'*-benzoic acid**, in the form of its lactone, **diphenyl-methylolid** (see below), m.p.  $92.5^\circ$ . This can also be obtained, in smaller yield, by the action of phosphorus oxychloride on sodium salicylate, and of phenol on the sulphate of *o*-diazobenzoic acid (*Graebe*, Ann. 284, 316). It corresponds in composition to **phenanthridone** (see below), m.p.  $293^\circ$ , which is obtained from diphenaminic acid (*Graebe*, Ann. 276, 245) by the action of bromine and caustic potash.



Diphenyl-methylolid



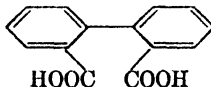
Phenanthridone

***p*-Hydroxyphenyl-*o'*-benzoic acid**,  $HO[4]C_6H_4C_6H_4[2']COOH$ , m.p.  $206^\circ$ , is formed, together with diphenylmethylolid and phenyl-salicylic acid by the action of phenol on diazotised anthranilic acid (*Graebe*, Ann. 284, 323).

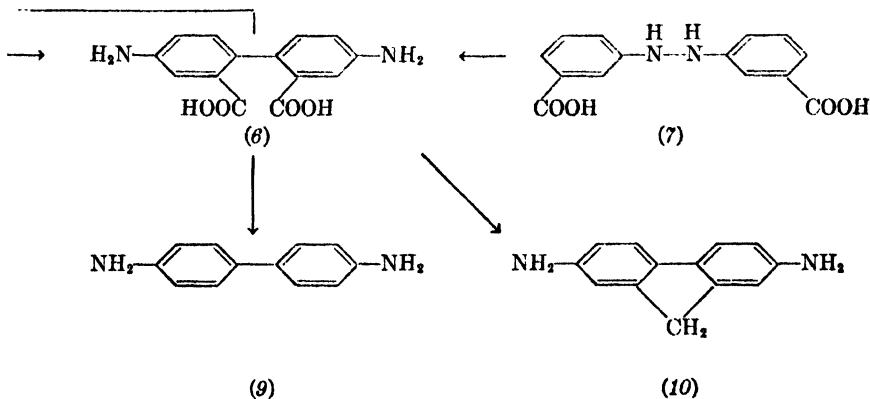
**Diphenyl-dicarboxylic acids** either contain the two carboxyl groups in the same or different rings. The most important diphenyl-dicarboxylic acid is **diphenic acid**.

***syn*-Phenyl-isophthalic acid**,  $C_6H_5C_6H_3[3,5](COOH)_2$ , melts above  $310^\circ$ , and is produced synthetically by boiling benzaldehyde and pyruvic acid with baryta water (cf. alkyl-isophthalic acids, p. 390) (*Doebner*, Ber. 24, 1750).

**Diphenic acid**, ***o, o'*-(2,2')-diphenyl-dicarboxylic acid**,  $COOH[2]C_6H_4[2']COOH$ , m.p.  $229^\circ$ ,



is formed from diazotised anthranilic acid by the action of ammoniacal cuprous oxide solution (*Vorländer*, Ann. 320, 123). Its dimethyl ester, m.p.  $74^\circ$ , is formed by heating *o*-iodobenzoic ester with copper (*Ullmann*, Ann. 332, 70); it is also formed by oxidation of phenanthraquinone (2) with chromic acid mixture or by boiling with alcoholic potash. The constitution of phenanthrene (1) follows from the constitution of the acid. The constitution of diphenic acid (4) follows from its oxidation to phthalic acid (*R. Anschütz* and *Japp*, Ber. 11, 211), and its formation by removing the amino-group from 4,4'-diamino-diphenyl-2,2'-dicarboxylic acid (6), which is produced on the one hand from 4,4'-dinitro-diphenic acid (5) and on the other by the isomerisation of *m*-hydrazo-benzoic acid (7) (*Schultz*, Ann. 204, 95):



To this cycle of reactions belongs also the formation of 4,4'-dinitrodiphenic acid by the oxidation of 2,7-dinitro-phenanthraquinone (8) and the transformation of diamino-diphenic acid (6) into benzidine (9), of which the constitution has been previously discussed (p. 497), and *p,p'*-diaminofluorene (10).

If diphenic acid is treated with conc. sulphuric acid it is converted into diphenylene-ketocarboxylic acid (p. 683). When warmed with acetyl chloride or

acetic anhydride it gives diphenic anhydride,  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CO} \end{array} \text{O}$ , m.p. 213° (Anschütz, Ann. 226, 1). Diphenyl chloride, m.p. 93°, is reduced by zinc and hydrochloric acid to phenanthrene-hydroquinone,  $\begin{array}{c} \text{C}_6\text{H}_4\text{C}(\text{OH}) \\ | \\ \text{C}_6\text{H}_4\text{C}(\text{OH}) \end{array}$  (Graebe, Ann. 247, 268). Diphenamic acid, m.p. 193°, gives phenanthridone (p. 505) with hypobromite or hypochlorite in alkaline solution (Graebe, Ann. 276, 248).

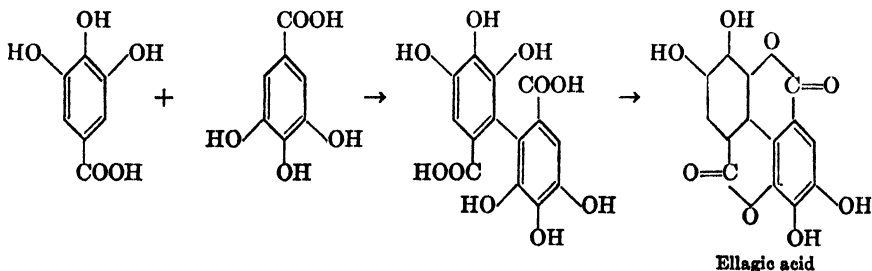


Diphenimide,  $(\text{C}_6\text{H}_4)_2(\text{CO})_2\text{NH}$ , m.p. 219°, see Graebe, Ann. 247, 271.

2-, 3-, and 4-Nitrodiphenic acids, m.p. 248-250° (decomp.), 268°, and 214-216°, respectively, 2,2'- and 4,4'-dinitrodiphenic acids, m.p. 303° (decomp.) and 253°, respectively, are obtained from nitro- and dinitro-phenanthraquinones by oxidation with chromic acid mixture; in the case of 2,2'- and 4,4'-dinitrodiphenic acids, the formation of anhydrides is difficult (Schmidt, Ber. 36, 3730, 3738). The ester of the 4,4'-acid is also formed by heating 2-bromo-5-nitrobenzoic ester with copper powder. In a similar way, 2,2'-dinitro-diphenyl-4,4'-dicarboxylic ester is obtained from 4-bromo-3-nitrobenzoic ester (Ullmann, Ber. 34, 2182). The nitrated diphenic acids give amino- and diamino-diphenic acids on reduction, from which amino-hydroxy and dihydroxy-diphenic acids can be obtained (Schmidt, Ber. 38, 3771) (see also p. 505).

**OPTICALLY ACTIVE NITRO-DIPHENIC ACIDS.** *o*-Mono- and *o,o'*-dinitro-diphenic acids are characteristic *o*-substituted diphenyl derivatives which can be resolved into optical antipodes, according to the phenomenon of molecular asymmetry discussed above (p. 495). The same is true of *o,p*-dinitro- and *o,p,o',p'*-tetranitrodiphenic acid. Those nitro-diphenic acids which contain two nitro-groups in the *o*-position are not racemised under quite energetic conditions, while those acids which have altogether only three *o*-substituents are racemised (Kuhn, Ann. 455, 272; 458, 221).

**Ellagic acid**, which is a constituent of numerous tannins, and is also found in the animal kingdom, is a dilactone of a hexahydroxy-diphenyl-2,2'-dicarboxylic acid. Ellagic acid can be synthesised by regulated oxidation of gallic acid, e.g., with arsenic acid (Graebe, Ber. 36, 212).



**Isodiphenic acid**, (*o,m'*)  $\text{COOH}[2]\text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3[3']\text{COOH}$ , m.p. 216°, is obtained from fluorenone-3-carboxylic acid by fusion with potash (Sieglitz, Ber. 54, 2070).

**2,4'-Diphenyl-dicarboxylic acid**,  $\text{COOH}[2]\text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3[4']\text{COOH}$ , m.p. 251°, is obtained from diphenylene (p. 498) (Reuland, Ber. 22, 3019).

**3,3'-Diphenyl-dicarboxylic acid**, m.p. 357°, **dimethyl ester**, m.p. 104°, is obtained by heating *m*-iodobenzoic ester with copper powder (Ullmann, Ann. 332, 71).

**4,4'-Diphenyl-dicarboxylic acid** decomposes at high temperatures. It is produced from benzidine and by oxidation of 4,4'-ditolyl. Its dimethyl ester, m.p. 212°, is obtained from methyl *p*-iodobenzoate, by the action of copper powder (Ullmann, Ann. 332, 73).

**4,4'-Diaminodiphenyl-3,3'-dicarboxylic acid** is obtained from *o*-nitrobenzoic acid in the same way as 4,4'-diaminodiphenic acid is obtained from *m*-nitrobenzoic acid (Loewenherz, Ber. 25, 2797; Bülow, Ber. 31, 2574). It is converted into **4,4'-dihydroxydiphenyl-3,3'-dicarboxylic acid** (or disalicic acid) through its *bis*-diazonium compound. The m.p. of disalicic acid is 302–305°.

**3,3'-Dimethyl-diphenyl-4,4'-dicarboxylic acid**, m.p. over 300°, is obtained from *o*-tolidine (p. 508), and gives **diphenyl-3,4,3',4'-tetracarboxylic acid**, **diphthalic acid**,  $(\text{COOH})_2[3,4]\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4[3',4'](\text{COOH})_2$ , on oxidation (Loewenherz, Ber. 26, 2486).

**2,2'-Dimethyl-diphenyl-5,5'-dicarboxylic acid**, m.p. over 300°, is obtained from *o*-iodo-*p*-tolunitrile by the action of copper powder and subsequent hydrolysis. It gives **2,5,2',5'-diphenyl-tetracarboxylic acid**, m.p. over 300°, on oxidation (Kenner, J. 103, 232). **2,3,2',3'-Diphenyl-tetracarboxylic acid**, m.p. 265°, see Kenner, J. 105, 2471.

For further polybasic diphenyl-carboxylic acids, and their connection with the corresponding phenanthraquinone derivatives, see Liebermann, Ber. 45, 1186; 46, 198.

## 2. DIPHENYL-BENZENES

Two diphenyl-phenylenes,  $\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2$ , are known: *m*-diphenyl-benzene, or isodiphenyl-benzene, m.p. 85°, b.p. 369°, and *p*-diphenyl-benzene, or terphenyl, m.p. 209–210°, b.p. 383°. They are produced together by passing benzene through a red-hot tube (Olgiati, Ber. 27, 3385), and by the action of phenyldiazonium chloride on diphenyl and aluminium chloride (Möhlau, Ber. 26, 1998). The *p*-compound is formed by the action of sodium on a mixture of *p*-dibromobenzene and bromobenzene (Wislicenus, Ann. 164, 168), from phenyldiazonium chloride and copper powder (Gerngross, Ber. 57, 739, 747), or from cyclohexyl bromide, benzene and aluminium chloride, with subsequent dehydrogenation with bromine (von Baun, Ber. 60, 1180). Isodiphenyl is best obtained from *m*-dichlorobenzene and chlorobenzene by the action of sodium in xylene (Chattaway, J. 69, 980). Terphenyl is also obtained by the distillation with zinc dust of many natural diphenyl-benzoquinone dyes (see below).

**1-Methyl-3,5-diphenyl-benzene**, m.p. 130°, is obtained from acetophenone and sodium ethylate at 130–140° (Gastaldi, Gazz. 45, I, 251).

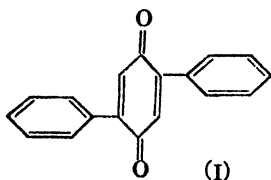
***p*-(2,4)-Diphenyl-phenol**,  $\text{C}_6\text{H}_5(\text{OH})[2,4](\text{C}_6\text{H}_5)_2$ , m.p. 194°, is formed by the condensation of cinnamic aldehyde and sodium phenylsuccinate with acetic anhydride, the diphenyl-butadiene-acetic acid,  $\text{C}_6\text{H}_5\text{CH}:\text{CH}:\text{C}(\text{C}_6\text{H}_5)\text{CH}_2\text{COOH}$ , formed intermediately, undergoing benzene ring condensation. The compound gives terphenyl on distillation with zinc dust (Fichter, Ber. 36, 1407).

***p*-Aminoterphenyl**, m.p. 198°, is obtained from diphenyl by the introduction of the *p*-aminophenyl radical by a synthesis due to Pummerer, which is capable of modification: the reaction of diphenyl with azobenzene hydrochloride in the presence of aluminium chloride (Pummerer, Ber. 55, 3105).

**2,6-Diphenyl-1,4-nitrophenol**,  $(\text{C}_6\text{H}_5)_2[2,6]\text{C}_6\text{H}_3[4]\text{NO}_2[1]\text{OH}$ , m.p. 136°, is obtained synthetically from dibenzyl ketone and nitromalonic aldehyde (see p. 25). It can be converted into the corresponding aminophenol, quinone, and hydroquinone (Hill, Am. Chem. J. 24, 1). These substances are also obtained from diphenyl-nitrosophenol, which is itself prepared, together with phenyl-nitrosophenol (p. 502) from nitroso-phenol and two molecules of phenyldiazonium chloride (Borsche, Ann. 312, 227).

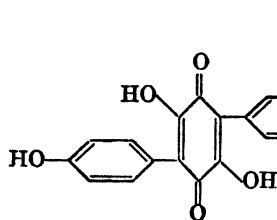
**Dibiphenyl, quaterphenyl**,  $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$ , m.p. 320°, is obtained from *p*-iododiphenyl and copper (Ullmann, Ann. 332, 52; Kuhn, Ann. 475, 131) or from phenyldiazonium chloride by decomposition with copper, when it is obtained together with diphenyl, terphenyl, and quinquiphenyl, m.p. 388.5°

(Graebe, Ber. 57, 739, 747). Sexiphenyl is obtained from *p*-iodoterphenyl by the action of silver, m.p. 475° (Pummerer, Ber. 57, 87).

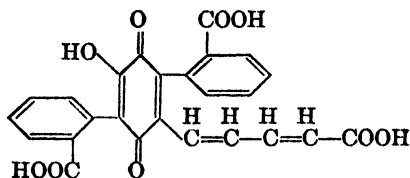


(I)

The red coloured 2,5-diphenylquinone (I), m.p. 214°, is produced from benzoquinone by treatment with benzene and aluminium chloride (Pummerer, Ber. 55, 3105). It is the parent substance of a series of fungus dyes, of which the constitution has been investigated by Kögl, whose results have been published in a number of papers. The brownish-violet polyporic acid from *Polyporus nidulans* is a 3,6-dihydroxy-2,5-diphenylquinone-1,4 (Kögl, Ann. 447, 78). The brown dye of *Paxillus atrotomentosus*, **atromentin**, is a tetrahydroxy-diphenylquinone (Kögl, Ann. 465, 211), which has also been prepared synthetically (Ann. 465, 243). The complex red pigment of *Amanita muscaria*, **muscarufin**, is a derivative of 2,5-diphenylquinone (see Vol. II, p. 425).



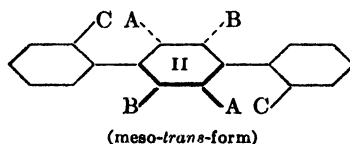
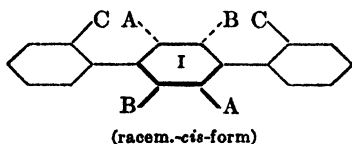
Atromentin



Muscarufin

### Atropism of the Terphenyls. *Cis-trans Isomeric Terphenyls*

In the diphenyl series, the space arrangement of the benzene nuclei gave rise to mirror-image isomerism when there were substituents in the ortho-positions (see p. 495). The same spatial considerations give rise, in the case of the *o*-derivatives of terphenyl, to the existence of atropic *cis*- and *trans*-forms, of which the *cis*-form (I) is resolvable into optical antipodes, whilst the *trans*-form (II) cannot be resolved, as it has a centre of symmetry:



For actual examples of this isomerism, see Adams, Am. 53, 343.

If the four substituents in the middle ring are the same, both the *cis*- and the *trans*-forms possess planes of symmetry, so that no active terphenyl of this type can be prepared. Examples of this type of isomerism are given by Adams (Am. 53, 2203).

### 3. TRIPHENYL-BENZENES, $C_6H_5(C_6H_5)_3$

Symmetrical or 1,3,5-triphenyl-benzene, m.p. 172°, is formed from acetophenone (p. 283) by heating with phosphorus pentoxide, or by passing hydrogen chloride into it, in the same way as mesitylene is formed from acetone (p. 25) (Mellin, Ber. 23, 2553), and also by heating phenyl-acetaldehyde with alcoholic potash (Stoermer, Ber. 38, 1965).

1,2,3-Triphenyl-benzene, m.p. 157° (Smith, Ber. 26, 69). Various hydro-

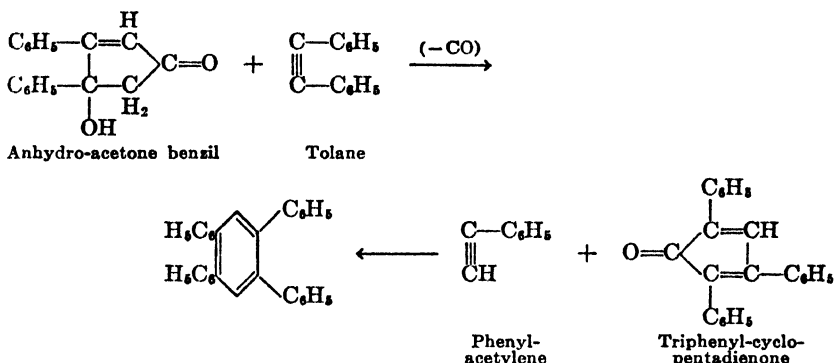
genated derivatives of 1,2,3-triphenyl-benzene have been prepared synthetically (Goldschmidt, Mo. 19, 706; Crossley, Proc. 20, 21; Mellin, Ber. 23, 2534).

3,3'-Diphenyl-diphenyl is obtained from 3-iodo-diphenyl and copper powder; m.p. 86°.

4,4'-Diphenyl-diphenyl, m.p. 320°, is obtained from 4-bromodiphenyl and copper powder (Bowden, J. 1931, 1111).

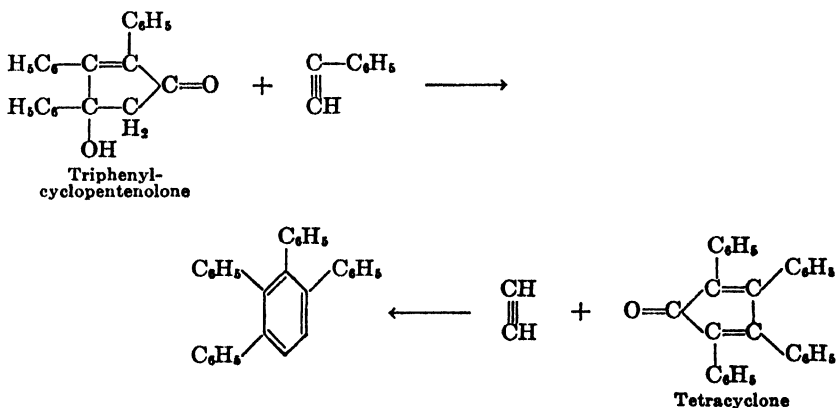
#### 4. TETRAPHENYL-BENZENES, $C_6H_2(C_6H_5)_4$

1,2,4,5-Tetraphenyl-benzene, m.p. 263–264° (corr. 269–270°), has been obtained by the application of *Diels' diene synthesis* in a perfectly straightforward way to the addition of tolane to anhydro-acetone-benzil, or of phenyl-acetylene to triphenyl-cyclopentadienone (Dillthey, Ber. 67, 2004):



1,2,4,5-Tetraphenyl-benzene is also produced by the action of phenyl-magnesium bromide on hexabromobenzene. Hexaphenyl-benzene is not produced in this reaction, as was formerly assumed (Durand, C.r. 191, 1460; Dillthey, Ber. 67, 495, 2004).

1,2,3,4-Tetraphenyl-benzene,  $C_6H_2(C_6H_5)_4$ , m.p. 190–191°, is obtained in an analogous way from triphenyl-cyclopentenolone and phenyl-acetylene, or from tetraphenyl-cyclopentadienone and acetylene (Dillthey, Ber. 66, 1627; 67, 2005).

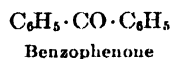
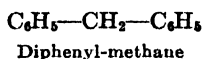


Pentaphenyl-benzene, m.p. 246° (corr. 251°), is obtained by condensation of tetraphenyl-cyclopentadienone with phenylacetylene (Dillthey, Ber. 67, 2005).

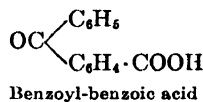
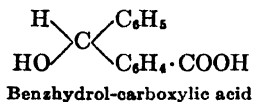
Hexaphenyl-benzene, m.p. 422° (corr. 449–450°) is produced by the condensation of tetraphenyl-cyclopentadienone with tolane (Dillthey, Ber. 67, 495).

## B. Polyphenyl Paraffins

The simplest hydrocarbon of this group is benzyl-benzene, or diphenylmethane, from which are derived the alkyl-diphenyl-methanes, and compounds which contain  $\text{NO}_2$ ,  $\text{NH}_2$ , or  $\text{OH}$  groups substituted in the benzene nucleus. If one of the hydrogen atoms of the  $\text{CH}_2$  group is replaced by  $\text{OH}$ , benzhydrol, or diphenyl-carbinol is formed. It is converted by oxidation into benzophenone or diphenyl-ketone. From the hydrocarbons, secondary alcohols, and ketones, of which the simplest members are:



are derived the corresponding carboxylic acids, *e.g.*,



### 1. BENZYL-BENZENE GROUP

#### (a) Hydrocarbons (Diphenylmethanes)

*Methods of preparation:*—1. From benzyl chloride, benzene, and zinc dust (*Zincke*, Ann. **159**, 374) or aluminium chloride (*Friedel and Crafts*). 2. From formaldehyde or methylene diacetate by the action of benzene and sulphuric acid (*Baeyer*, Ber. **6**, 963). 3. From benzyl benzene-sulphonate by boiling with benzene (*Földi*, Ber. **61**, 1609). The above reactions are capable of extensive generalisation; thus, by the second method, numerous hydrocarbons have been obtained by using other aldehydes in place of formaldehyde, such hydrocarbons containing two benzene nuclei attached to the same carbon atom (see *as*-diphenyl-ethane, p. 552). Benzyl alcohol will also condense with benzene under the action of concentrated sulphuric acid, giving diphenylmethane (*Baeyer*, Ber. **6**, 963). In the case of the third reaction mentioned above, the benzene can be replaced by certain derivatives or homologues. 4. By reduction of ketones into which the benzyl-benzenes are converted by oxidation.

Diphenylmethane derivatives are obtained as by-products: 5. by the action of sodium on mixtures of bromobenzenes and alkylbenzenes (see p. 494 and *Weiler*, Ber. **33**, 334); 6. by the oxidation of alkyl-benzenes with manganese dioxide and sulphuric acid. Tolyphenyl-methane is formed from toluene (*Weiler*, Ber. **33**, 464).

**Diphenylmethane, benzyl-benzene**,  $\text{CH}_2(\text{C}_6\text{H}_5)_2$ , m.p.  $26^\circ$ , b.p.  $261^\circ$ , is formed: 1. from benzyl chloride and benzene by the action of zinc dust or aluminium chloride; 2. from methylene chloride, benzene, and aluminium chloride; 3. from methylal, or 4. benzyl

alcohol, benzene, and sulphuric acid; 5. from benzyl benzene-sulphonate and benzene; 6. by reduction of benzophenone with zinc dust, or zinc and sulphuric acid, or phosphorus and hydriodic acid; 7. from diphenylacetic acid (p. 555) by distillation with soda-lime (*Jena*, Ann. 155, 86).

Diphenylmethane smells of oranges and geraniums. When passed through a red-hot tube it is converted into diphenylene-methane or fluorene (p. 678). Chromic acid oxidises it to benzophenone (p. 515). With concentrated nitric acid it gives *p,p'*- and *o,p'*-dinitro- and tetranitro-diphenylmethane (*Staedel*, Ann. 283, 154).

**BENZYL TOLUENES, PHENYL-TOLYL-METHANES**,  $C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot CH_3$ . By the action of zinc dust on a mixture of benzyl chloride and toluene an inseparable mixture of *o*- and *p*-benzyl-toluene is obtained, together with anthracene (p. 645). Pure *p*-benzyl-toluene, b.p. 272–274°, is obtained by heating *p*-tolyl-phenyl-ketone with zinc dust or from benzyl-benzene-sulphonate and toluene; it also appears to be produced, together with *p*-ditolyl (p. 494), by the action of sodium on *p*-bromotoluene. In the same way, a pentamethyl-diphenylmethane is obtained together with dimesityl from bromomesitylene and sodium (see above).

Benzyl-*p*-xylene, b.p. 294°. Benzyl-mesitylene, m.p. 36°, b.p. 301°. Benzyl-durenes, m.p. 60°, b.p. 310°, and m.p. 145°, b.p. 326°, respectively. Benzyl-pentaethyl-benzene, m.p. 88°. *p,p'*-Ditolyl-methane, m.p. 22°, b.p. 286°. Dimesityl-methane, m.p. 139°. The unsymmetrical hydrocarbons are obtained by methods 1 and 5, and the symmetrical ones by method 1 (*Fournier*, Bull. [3], 7, 653).

*o*-Chloro-diphenylmethane, m.p. 13.2°, b.p. 164.5° (9 mm.). *p*-Chloro-diphenylmethane, m.p. 7.5°, b.p. 160° (11 mm.). Both are obtainable from their carbinols by reduction with hydriodic acid (*Tshitshibabin*, C. 1926, I, 919).

**NITRO-DIPHENYLMETHANES** (*Staedel*, Ann. 283, 157). *o*-Nitrobenzyl-benzene, a liquid, is obtained from *o*-nitrobenzyl chloride, benzene, and aluminium chloride (*Geigy*, Ber. 18, 2402; *Gabriel*, Ber. 29, 1303). *m*-Nitrobenzyl-benzene, a liquid, and *p*-nitrobenzyl-benzene, m.p. 31°, are obtained from the corresponding nitrobenzyl alcohols, benzene and sulphuric acid (*Basler*, Ber. 16, 2716).

*o,o'*-Dinitro-diphenylmethane, m.p. 159°, is obtained from *p,p'*-diamino-*o,o'*-dinitrodiphenylmethane by removal of the amino-groups (*Bertram*, J. pr. (2), 65, 327).

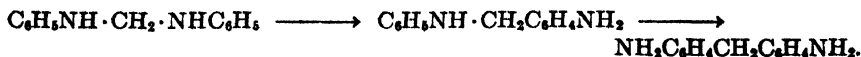
*m,m'*-Dinitro-diphenylmethane, m.p. 174°, is obtained from nitrobenzyl alcohol and nitrobenzene, or from formaldehyde by the action of nitrobenzene and conc. sulphuric acid (*Gettermann*, Ber. 27, 2293; *Schopff*, Ber. 27, 2321). *m,p'*-Dinitro-diphenylmethane, *p*-nitrobenzyl-*m*-nitrobenzene, m.p. 103°. *p,p'*-Dinitro-diphenylmethane, m.p. 183°, is obtained from diphenylmethane together with *o,p'*-dinitro-phenylmethane, m.p. 118° (*Staedel*, Ber. 27, 2110; Ann. 194, 363). Tetranitro-diphenylmethane, m.p. 172°, gives dark blue salts with alkalis (*Richter*, Ber. 21, 2475).

**AMINO-DIPHENYLMETHANES**. *o*-Amino-diphenylmethane is a liquid which is converted into acridine on passing its vapour over red-hot lead oxide, and into fluorene (p. 678) on treatment with nitrous acid (*Fischer*, Ber. 27, 2786). *m*- and *p*-amino-diphenylmethane, m.p. 46° and 34°, respectively (*Basler*, Ber. 16, 2718).

*o,o'*-Diamino-diphenylmethane, m.p. 160°, see *Bertram*, J. pr. [2], 65, 331.

*o,o'*-Dichloro-*o,o'*-diamino-diphenylmethane, m.p. 110°, is produced by the action of formaldehyde on *o*-chloroaniline, and subsequent treatment of the base formed with hydrogen chloride (*Mayer*, Ber. 47, 1161).

*p,p'*-Diamino-diphenylmethanes. These are produced from methylene-dianilines (p. 83) by heating with aniline salts; in this reaction aminobenzyl-aniline must be formed as an intermediate product (p. 262), and is then transformed into diamino-diphenylmethane:





This mechanism for the reaction is confirmed by the ready formation of diamino-diphenylmethanes from amino-benzyl-anilines by heating with aniline salts (Ger. Pat. 107,718; cf. Meyer, Ber. 33, 250).

*p,p'*-Diamino-diphenylmethane, m.p. 85°, is converted on heating with aniline or *p*-toluidine with addition of an oxidising agent, into pararosaniline or rosaniline (Gram, Ber. 25, 303).

*N,N'*-Tetramethyl-*p,p'*-diamino-diphenylmethane, m.p. 91°, is produced by heating dimethylaniline with methylene iodide, chloroform, or carbon tetrachloride, and also by the action of formaldehyde and hydrochloric acid (Möhlau, Ber. 35, 359), methylal, or carbon disulphide and zinc on dimethylaniline. The hydrogen of the CH<sub>3</sub> group attached to the basic radical is readily replaced by sulphur; see *p,p'*-tetramethyl-diamino-thiobenzophenone (p. 519). Isomeric diamino-diphenylmethanes, see Staedel, Ann., 283, 149. *p,p'*-Diamino-*o,o'*-dinitrodiphenylmethane, and its reduction products, see Duval, Bull. [4], 7, 527. *p,p'*-Dihydrazino-diphenylmethane, CH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>·NHNH<sub>2</sub>)<sub>2</sub>, m.p. 140°, see Fenger, J. pr. [2] 74, 155.

**HYDROXY-DIPHENYLMETHANES.** *o*-Benzyl-phenol, b.p. 303–307°, is produced by acting on benzyl benzene-sulphonate with phenol (Földi, Ber. 61, 1609). *p*-Benzyl-phenol is formed by the same reaction; m.p. 84°, b.p. 325° (in a current of carbon dioxide). This is formed, like the *o*-compound, by the following reactions: 1. From benzyl chloride, phenol, and zinc (Bakunin, Gazz. 33, II, 454). 2. From benzyl alcohol, by the action of phenol, and conc. sulphuric acid or zinc chloride. 3. From *p*-aminodiphenylmethane. The bromination products of these phenols are in part readily converted into methylene-quinones, e.g., C<sub>6</sub>H<sub>5</sub>CH:C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>:O + H<sub>2</sub>O, in a similar way to the brominated phenolic alcohol bromides. The methylene-quinone is a yellow precipitate, which is readily converted into dibromo-hydroxy-benzhydrol (Zincke, Ann. 334, 367).

**AMINO-BENZYLPHENOLS** are readily obtained by the condensation of amino-benzyl-alcohols with phenols (Friedländer, Mo. 23, 973). *p*-Dialkyl-amino-benzylphenols, e.g., C<sub>6</sub>H<sub>4</sub>OHBBr<sub>2</sub>·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>[4]N(CH<sub>3</sub>)<sub>2</sub>, is obtained by the action of *o*- and *p*-pseudophenol bromides (p. 339) on tertiary anilines.

*o,o'*-Dihydroxy-diphenylmethane is known only in the form of its anhydride, xanthene. *p,p'*-Dihydroxy-diphenylmethane, m.p. 158°, is obtained by fusing diphenylmethane disulphonic acid with caustic potash. Its dimethyl ether, m.p. 52°, is obtained by the action of concentrated sulphuric acid on a solution of anisole and methylal in glacial acetic acid. By exhaustive bromination it is converted into a heptabromide, which easily loses HBr giving a methylene quinone, O:C<sub>6</sub>Br<sub>2</sub>H:CHC<sub>6</sub>BrH<sub>2</sub>(OH), red needles, m.p. 245° (Hindushka, J. pr. [2], 58, 441; Zincke, Ann. 330, 61). Substituted *p,p'*-dihydroxy-diphenylmethanes have been obtained by various methods from *p*-hydroxybenzyl alcohols and the pseudophenol halides derived from them (Auwers, Ann. 356, 124).

*o,p*-Dihydroxy-diphenylmethane, m.p. 76–77°, is produced from benzyl chloride and resorcinol in nitrobenzene and aluminium chloride, or by the reduction of *o,p*-dihydroxy-benzophenone (Klarman, Am. 48, 791).

Polyhydric phenols very readily condense with formaldehyde to give polyhydroxy-diphenylmethanes: Methylene-diccatechol, m.p. 220° (decomp.) (Caro, Ber. 26, 254). Methylene-diresorcinol, methylene-diortcinol, methylene-diphloroglucinol, see Borhm, Ann. 329, 269; see also pp. 225, 230.

When treated with acetone, cresols are converted into derivatives of β,β-dicresyl-propane, HO(CH<sub>2</sub>)·C<sub>6</sub>H<sub>3</sub>—C(CH<sub>3</sub>)<sub>2</sub>—C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)OH (Zincke, Ann. 400, 33).

### (b) Alcohols (Benzhydrols)

Diphenylcarbinol, benzhydrol, HO·CH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, m.p. 68°, b.p. 298° (decomp. into water and benzhydrol-ether, O[CH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, m.p. 109°) (Kostanecki, Ber. 34, 1695). Diphenylcarbinol is produced from diphenyl-bromomethane by heating with water to 150°, but more easily from benzophenone by the action of sodium amalgam, or by catalytic reduction with a nickel catalyst (Adkins, Am. 52, 4349), or, together with benzpinacene by heating with alcoholic potash and zinc dust (Zagoumenny, Ann. 184, 174). It is synthesised from ethyl formate and phenyl magnesium bromide (Masson, C.r. 135, 533). It is also obtained from benzaldehyde and phenyl magnesium iodide, which can be prepared in benzene

solution from iodobenzene and magnesium in the presence of some dimethylaniline (*Tschelintzeff*, Ber. 37, 4539). It is also produced in the electrolytic reduction of benzophenone in alcoholic sodium acetate solution (*Elbs*, Z. elektrochem. 7, 644; 8, 784). For the yield obtained by reduction of benzophenone under different conditions, see *Böseken*, Akad. Wetens. Amsterdam, 16, 91. On oxidation it is converted into benzophenone, and also on heating in the presence of palladium black (*Knoevenagel*, Ber. 36, 2816). Diphenylcarbinol condenses with quinones and quinonoid substances, one or two  $\text{CH}(\text{C}_6\text{H}_5)_2$  groups entering the quinoid nucleus (*Möhlau*, Ber. 32, 2146; 33, 799). By hydrogenation with  $\text{H}_2/\text{Pt}$  in acetic acid under pressure, dicyclohexylmethane is produced (*Levene*, J. Biol. Chem. 89, 471). Phenyl-*p*-tolyl-carbinol, m.p.  $52^\circ$  (*Fischer*, Ann. 194, 265); for further methylated and halogenated diphenylcarbinols, see *Cohen*, Rec. 38, 113 and *Montagne*, Rec. 41, 703.

Diphenylcarbinol chloride, diphenyl-chloromethane, m.p.  $14^\circ$ , is obtained from diphenylcarbinol and hydrochloric acid, or from diphenylmethane by heating with phosphorus pentachloride. It decomposes on heating into hydrogen chloride and tetraphenyl-ethylene (p. 574) (*Engler*, Ber. 7, 1128). Diphenylbromomethane, m.p.  $45^\circ$ , obtained from diphenylmethane and bromine gives benzhydrol-ether when treated with zinc oxide (*Auger*, Bull. [3], 23, 336).

Benzhydrylamine,  $\text{NH}_2\text{CH}(\text{C}_6\text{H}_5)_2$ , b.p.  $288^\circ$ , is obtained from diphenylbromomethane and from benzophenone oxime (*Goldschmidt*, Ber. 19, 3233; *Tafel*, Ber. 35, 1515; *Konovalov*, C. 1901, I, 1002). Homologous alkyl-benzhydrylamines are prepared by the latter method (*Goldschmidt*, Ber. 24, 2797). Formyl derivative, m.p.  $132^\circ$ , is obtained from benzophenone and ammonium formate at  $200\text{--}250^\circ$  (*Lenckart*, Ber. 19, 2129). Formamidine-benzhydryl,  $\text{CH}(\text{NH})\text{NHCH}(\text{C}_6\text{H}_5)_2$ , is formed from hydrocyanic acid, hydrochloric acid, benzene and aluminium chloride (see p. 343) (*Gattermann*, Ber. 31, 1771). Dibenzhydrylamine, m.p.  $136^\circ$ . Phenylbenzhydrylamine,  $\text{C}_6\text{H}_5\text{NH}\cdot\text{CH}(\text{C}_6\text{H}_5)_2$ , b.p.  $233^\circ$  (20 mm.), is obtained by the addition of phenyl magnesium bromide to benzylidene aniline, and decomposing the product with acids (*Busch*, Ber. 38, 1767).

$\beta$ -Benzhydrylhydroxylamine,  $\text{HO}\cdot\text{NH}\cdot\text{CH}(\text{C}_6\text{H}_5)_2$ , m.p.  $78^\circ$ , is obtained by boiling a solution of diphenyl-bromomethane and acetoxime with glacial acetic acid and water (*Behreur*, Ann. 278, 364).

Benzhydrylhydrazine,  $(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{NHNH}_2$ , m.p.  $59^\circ$ , b.p.  $188^\circ$  (12 mm.), and *sym-bis*-benzhydrylhydrazine,  $(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{NHNH}\cdot\text{CH}(\text{C}_6\text{H}_5)_2$ , m.p.  $133^\circ$ , are obtained from benzophenone hydrazone and *bis*-benzophenone hydrazone (p. 517) by reduction with sodium amalgam and alcohol. Benzhydrylhydrazine decomposes on boiling with hydrochloric acid into diphenyl-chloromethane and hydrazine (*Darefsky*, J. pr. [2], 67, 112).

*o*-Aminobenzhydrol,  $\text{C}_6\text{H}_4\begin{cases} \text{CH}(\text{OH})\text{C}_6\text{H}_5 \\ \text{NH}_2 \end{cases}$ , m.p.  $120^\circ$ , is prepared by reduction of *o*-aminobenzophenone. It is capable of forming heterocyclic compounds in a similar way to *o*-aminobenzyl alcohol (p. 262) (*Gabriel*, Ber. 29, 1304). The isomeric *o*-hydroxybenzhydrylamine,  $\text{C}_6\text{H}_4\begin{cases} \text{CH}(\text{NH}_2)\text{C}_6\text{H}_5 \\ \text{OH} \end{cases}$ , m.p.  $103^\circ$ , is obtained

by the reduction of phenylindoxazene (*Cohen*, Osterr. Chem.-Ztg. 1, 137).

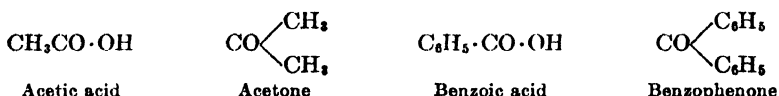
*p*-Hydroxybenzhydrol,  $\text{HO}[4]\text{C}_6\text{H}_4\text{CH}(\text{OH})\text{C}_6\text{H}_5$ , m.p.  $161^\circ$ , is obtained by the reduction of *p*-benzoyl-phenol (*Doebner*, Ann. 210, 253). *o,p*-Dihydroxybenzhydrol is obtained by the condensation of benzaldehyde with resorcinol and alkali (*Pope*, J. 97, 98). *o,o',p,p'*-Tetramethoxybenzhydrol, m.p.  $179^\circ$ , is obtained from *vic*-iodoresorcinol dimethyl ether, magnesium, and ethyl formate (*Baeyer*, Ann. 372, 128).

By the aldol condensation of benzaldehyde, or *p*-nitrobenzaldehyde and anilines, especially dimethylaniline, with a little hydrochloric acid (if zinc chloride or oxalic acid is used triphenylmethane derivatives result) the following compounds are produced: *p*-nitro-*p'*-amino benzhydrol,  $\text{NO}_2\text{C}_6\text{H}_4\text{CH}(\text{OH})\text{C}_6\text{H}_4\text{NH}_2$  (Ger. Pat. 119,461), *p*-dimethylaminobenzhydrol,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ , m.p.  $69^\circ$ , and *p*-dimethylamino-*p'*-nitrobenzhydrol, m.p.  $96^\circ$  (*Albrecht*, Ber. 21, 3293). This compound gives *p*-dimethylamino-*p*-amino-diphenylmethane, m.p.  $165^\circ$ , on reduction.

*p,p'*-Tetramethyldiamino-benzhydrol, m.p. 96°, is obtained by the reduction of *p,p'*-tetramethyldiamino-benzophenone, and by the oxidation of tetramethyldiamino-diphenylmethane with lead dioxide (Möhlau, Ber. 35, 359). On heating with dilute acids it is decomposed to dimethylaniline and dimethylamino-benzaldehyde (Weil, Ber. 27, 3316). In the solid state *p,p'*-tetramethyldiamino-benzhydrol is white, but in solution it is blue (V. Meyer, Ber. 20, 1733, note). In acid solution the substance has a quinoid structure, possibly similar to that of auramine (p. 519) (Hinsberg, Ber. 30, 2803; Hantzsch, Ber. 33, 283). It is a very reactive substance. On standing or boiling with alcohol, ethers are produced; the methyl ether,  $\text{CH}_3\text{OCH}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2$ , has m.p. 72° (Fischer, C. 1902, I, 471). With hydrogen sulphide in alcoholic solution it gives tetramethyldiamino-benzthiohydrol,  $\text{HS}\cdot\text{CH}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2$ , m.p. 82°. With aromatic amines it reacts spontaneously giving tetramethyldiamino-benzhydrylarylamines,  $\text{ArNHCH}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2$ , or aryl-leucauramines. The simplest leucauramine,  $\text{NH}_2\text{CH}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2$ , m.p. 135°, is obtained from auramine (p. 519) by reduction with sodium amalgam and alcohol; on oxidation, auramine is regenerated. With ammonium sulphide, the leucauramines give tetramethyldiamino-benzhydryl-sulphide,  $\text{S}[\text{CH}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2]_2$ , m.p. 172° (Möhlau, Ber. 35, 375; Gnehm, Ber. 35, 913). With compounds which contain a reactive  $\text{CH}_2$  group, such as malonic ester, acetoacetic ester, etc., the hydrol combines readily with elimination of water (Fosse, Ann. chim. phys. [8], 18, 400). With quinones and quinoid substances it condenses in a similar manner to benzhydrol (p. 513; Möhlau, Ber. 34, 881, etc.).

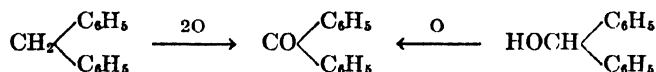
### (c) Ketones (Benzophenones)

The ketones of the diphenylmethane group bear the same relationship to benzoic acid as the acetones do to the fatty acids:



This relationship is made evident in various ways in the methods of preparation of these compounds.

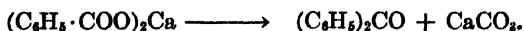
*Methods of formation.*—1. By oxidation (a) of diphenylmethanes, and (b) the diphenylcarbinols by chromic acid:



If the  $\text{CH}_2$  group contains alkyls or carboxyl, these groups are eliminated in the oxidation giving rise to the ketone; if the benzene radicals contain alkyl groups these are oxidised to carboxyl.

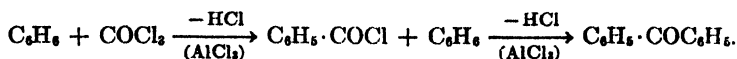
2. From the ketone-chlorides (see diphenyl-dichloromethane, p. 516), by hydrolysis with hot water.

*Nuclear syntheses.*—3. By distillation of the calcium salts of mononuclear aromatic monocarboxylic acids, in which the carboxyl groups are directly attached to the nucleus:



4. By the condensation of benzoic acid, or benzoic anhydride with benzene by heating with phosphorus pentoxide.

5. By the action of benzoyl chloride, or phosgene on benzene in the presence of aluminium chloride. In the second case acid chlorides are produced first, and are then converted into ketones (Friedel, Ber. 10, 1854):



6. By the action of carbon tetrachloride on aromatic hydrocarbons and their halogen substitution products, in the presence of aluminium chloride, benzophenone chlorides are produced, which, on heating with water, are converted into the ketones (*Norris*, *Am. Ch. J.* 30, 392; *Böeseken*, *Rec.* 24, 1).

7. By the action of mercury diphenyl on acid chlorides, such as benzoyl chloride.

*Properties.*—1. On heating with zinc dust or hydriodic acid and red phosphorus, the ketones are reconverted into the hydrocarbons. Thus, diphenylmethane is produced from benzophenone. 2. By the action of sodium amalgam, the ketones are converted into secondary alcohols (benzhydrols) and pinacones. 3. With the alkali metals they form the metallic ketyls (see Vol. IV).

4. Alkylated benzophenones are broken down by heating with phosphoric acid, hydrochloric or hydriodic acids into hydrocarbons and carboxylic acids (see *Klages*, *Ber.* 32, 1565; *Weiler*, *Ber.* 32, 1908).

**Benzophenone, diphenyl-ketone**,  $\text{CO}(\text{C}_6\text{H}_5)_2$ , b.p.  $307^\circ$  (b.p.  $162^\circ$  (12 mm.)), is known in two modifications. The labile form, m.p.  $26^\circ$ , is produced by boiling, or by the action of air on solutions of the stable modification, m.p.  $46^\circ$ , into which the labile form usually passes spontaneously with a marked evolution of heat in the presence of a trace of the stable form (*Tanatar*, *Ber.* 26, R 380; *Schaum*, *Z. physikal. Chem.* 25, 722). It is produced by the general methods of preparation: 1. from diphenylmethane, *as*-diphenylethane (p. 552), benzhydrol, diphenylacetic acid (p. 555), *etc.*, by oxidation; 2. from diphenyl-dichloromethane; 3. by distillation of calcium benzoate (*Péligot*, *Ann.* 12, 41); 4. from benzoic acid and benzene by the action of phosphorus pentoxide; 5. from phosgene, or benzoyl chloride, benzene, and aluminium chloride; 6. from benzoyl chloride and mercury diphenyl, and together with benzoic acid and triphenylcarbinol; 7. by the action of carbon dioxide on phenyl magnesium bromide (*Schroeter*, *Ber.* 36, 3005); 8. by removal of the  $\text{COOH}$  group from *o*-benzoyl-benzoic acid (*Dougherty*, *Ann.* 50, 571); on fusion with alkali it decomposes to benzoic acid and benzene, and on heating with sodamide in benzene solution it gives benzamide and benzene (*Haller*, *C.r.* 147, 824); 9. from chlorobenzene, benzonitrile and sodium (*Morton*, *Am.* 53, 2769); 10. from benzonitrile and phenyl magnesium bromide (*Mevrodin*, *C.r.* 191, 1064); 11. by the oxidation of diphenylmethane (*Ger. Pat.* 539,476).

On reduction, benzophenone gives diphenylmethane, diphenylcarbinol, and benzpinacol (p. 574). The reduction to diphenylcarbinol is effected by alcoholic potash; on the effect of substituents on the course of this reaction, see *Montagne*, *Ber.* 49, 2243. **Hexahydrobenzophenone**, m.p.  $54^\circ$ , is obtained from hexahydrobenzoyl chloride, benzene, and aluminium chloride (*Meyer*, *Ber.* 30, 1940).

**HOMOLOGOUS BENZOPHENONES.** *o*-Tolyl-phenyl-ketone, b.p.  $315^\circ$ , when passed over hot lead oxide is converted into anthraquinone (p. 657), and when heated with zinc dust it gives anthracene (p. 645) (*Behr*, *Ber.* 6, 754). *m*-Tolyl-phenyl-ketone, b.p.  $314^\circ$ . *p*-Tolyl-phenyl-ketone is known in two modifi-

cations; labile form, m.p. 55°, hexagonal; stable form, m.p. 59°, monoclinic (*Thörner*, Ann. 189, 84; *Ador*, Ber. 12, 2299). *p*-Ditolyl-ketone, m.p. 92°, b.p. 333°. Benzoyl-xylene, m.p. 36°, b.p. 317° (*Elbs*, Ber. 17, 2847). Benzoyl-mesitylene, m.p. 36°, b.p. 317°, mesitoyl-mesitylene, m.p. 85° (*Elbs*, J. pr. [2], 35, 486; *Weiler*, Ber. 32, 1910). See also *Cohen*, Rec. 38, 113; *Morgan*, J. 1929, 2203, 2551. These compounds are most conveniently prepared by method 5.

1,3,5-Tribenzoyl-benzene, 1,3,5-(C<sub>6</sub>H<sub>5</sub>·CO)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>, m.p. 118–119°, is obtained from hydroxymethylene-acetophenone by boiling with glacial acetic acid (p. 26) (*Claisen*, Ber. 26, 729).

**DERIVATIVES OF BENZOPHENONE IN WHICH OXYGEN IS REPLACED: BENZOPHENONE CHLORIDE, DIPHENYL-DICHLOROMETHANE**, CCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, b.p. 193° (30 mm.), is obtained from benzophenone by the action of phosphorus pentachloride, and by the action of benzene on carbon tetrachloride in the presence of aluminium chloride (*Bösesen*, Rec. 24, 1). On heating with water it is converted into benzophenone, and with silver or zinc dust it gives tetraphenyl-ethylene (p. 574),  $\alpha$ - and  $\beta$ -benzpinacoline (*Lohse*, Ber. 29, 1790). By the action of 2 mols. of sodamide it gives N,  $\alpha$ -diphenyl-tetrazole,

$$\text{C}_6\text{H}_5\text{C} \begin{array}{c} \diagup \text{N}(\text{C}_6\text{H}_5) \cdot \text{N} \\ \diagdown \text{N} \end{array} \text{N}$$
, nitrogen being eliminated (*Schroeter*, Ber. 42, 3359).

Benzophenone bromide is obtained by adding bromine drop by drop to diphenyl-methane at 150°.

Acetals of benzophenone have been obtained from benzophenone chloride by the action of sodium alcoholates, and from benzophenone and orthoformic esters (p. 283): benzophenone-dimethyl- and -diethyl-acetal, m.p. 107° and 52°, respectively, b.p. 289° and 295°, respectively (*Claisen*, Ber. 29, 2932; *Mackenzie*, J. 69, 985).

Thiobenzophenone, CS(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, m.p. 51–52°, b.p. 165–169°, is obtained by the action of thiophosgene, CSCl<sub>2</sub>, on benzene in the presence of aluminium chloride. The corresponding phenolic ether reacts more readily than the hydrocarbon in this reaction (*Gattermann*, Ber. 28, 2869). Thiobenzophenone is also produced by the action of phosphorus sulphide, or hydrogen sulphide and hydrochloric acid (*Staudinger*, Ber. 61, 1576) on benzophenone, or by the action of alcoholic potassium sulphide solution or thioacetic acid on benzophenone chloride (*Schönberg*, Ber. 61, 1375). It is a blue oil which crystallises at low temperatures to blue needles. It can be separated from benzophenone by its addition compound with diphenyl-ketene. Thiobenzophenone is capable of autoxidation. On heating to 160–170°, it breaks down into tetraphenyl-ethylene and sulphur (*Staudinger*, Ber. 61, 1576).

Benzophenone-diethyl- and -dibenzyl-mercaptol, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, m.p. 144°, give the corresponding sulphonals on careful oxidation, m.p. 137° and 208°, respectively (*Posner*, Ber. 35, 2343).

Diphenyl-dinitromethane, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(NO<sub>2</sub>)<sub>2</sub>, m.p. 78°, is obtained by acting on a solution of benzophenone oxime in ether with nitrogen tetroxide. It is reconverted into benzophenone oxime by reduction with zinc dust and acetic acid, benzhydrylamine being also formed (*Scholl*, Ber. 23, 3490).

Iminobenzophenone, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=NH, is a colourless oil obtained by the action of ammonia on an alcoholic solution of benzophenone (*Thomas*, Ar. Pharm. 243, 395), or from benzophenone oxime by heating in a current of an indifferent gas. Its hydrochloride is produced by heating benzophenone chloride with urethane to 130°. It rapidly sublimes at 250° and is readily decomposed by cold water into benzophenone and ammonium chloride. Phenyl-benzal-sultim,

$$\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{C}(\text{C}_6\text{H}_5) \\ \diagdown \text{SO}_2 \end{array} \text{N}$$
, m.p. 164°, is to be regarded as a derivative of iminobenzophenone. It is produced by the condensation of pseudo-saccharin chloride (p. 334) with benzene in the presence of aluminium chloride (*Fritsch*, Ber. 29, 2296).

Phenyl-iminobenzophenone, benzophenone-anil, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=N·C<sub>6</sub>H<sub>5</sub>, m.p. 116°, is prepared from benzophenone chloride and aniline (*Pauli*, Ann. 187, 199), or from benzophenone and aniline at 240–250°, and by the action of phenyl magnesium bromide on phenyl-iminobenzoic ester, C<sub>6</sub>H<sub>5</sub>C(OCH<sub>3</sub>):NC<sub>6</sub>H<sub>5</sub> (*Marquis*, C.r. 142, 711). It forms unstable salts with acids, and an addition product with

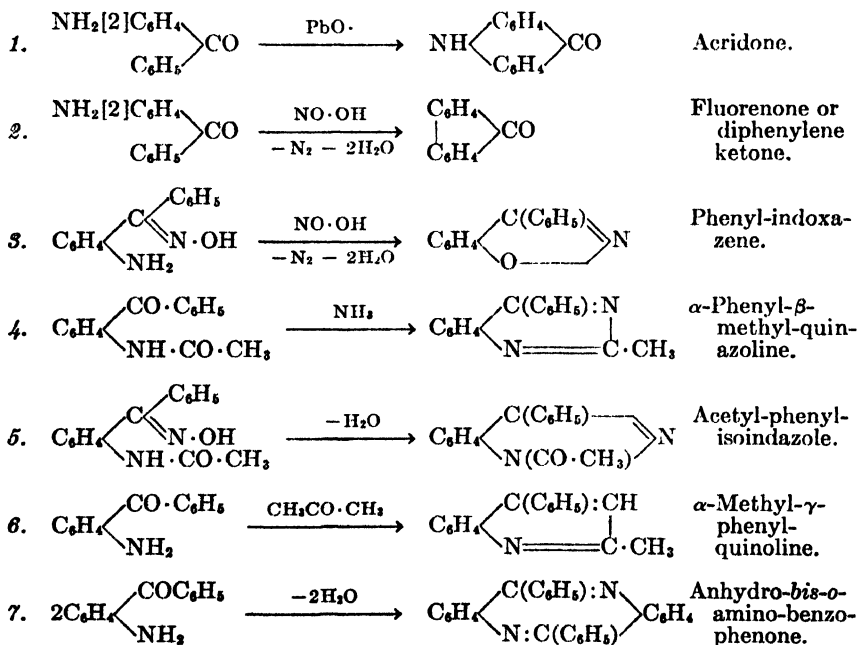


2,2'- and 2,3'-dinitrobenzophenone are formed (*Staedel*, Ann. 283, 164; *Ber.* 27, 2111). 2,2',4,4'-Tetranitrobenzophenone, m.p. 225° (*Schopff*, *Ber.* 27, 2318). Further substituted benzophenones are described in *Limpricht*, Ann. 286, 306, and *Consonno*, Gazz. 34, I, 374.

*o*-Phenyl-anthranil,  $\text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)\text{N}$ , faint yellow crystals, m.p. 53°, may

be regarded as an inner anhydride of *o*-hydroxylamino-benzophenone. It is produced in a similar way to anthranil (p. 278) and *C*-methyl-anthranil, by the reduction of *o*-nitrobenzophenone with tin and acetic acid, or by the oxidation of *o*-aminobenzophenone with permonosulphuric acid (*Bamberger*, *Ber.* 42, 1723) as well as in smaller quantities by the condensation of *o*-nitrobenzaldehyde with conc. sulphuric acid (*Kliegl*, *Ber.* 41, 1845). When heated under ordinary pressure it isomerises to acridone (*Kliegl*, *Ber.* 42, 592). The same transformation also occurs when the substance is acted upon simultaneously by concentrated sulphuric and nitrous acids, apparently with intermediate formation of nitroso-*o*-hydroxylamino-benzophenone (*Bamberger*, *Ber.* 42, 1716); cf. the analogous fission of anthranil (p. 278) and the transformation of *C*-methyl anthranil into indoxyl (p. 286). A series of compounds obtained by condensation of *o*-nitrobenzaldehyde and tertiary amines and phenols with concentrated hydrochloric acid are to be regarded as derivatives of phenyl-anthranil (*Bamberger*, *Ber.* 42, 1714).

AMINO-BENZOPHENONES are formed from the nitrobenzophenones, from benzoic acid by the action of dimethylaniline and phosphorus pentoxide, benzoyl chloride, phthalanil, and zinc chloride (*Doebner*, *Ber.* 14, 1838), etc., *o*-, *m*-, and



*p*-amino-benzophenone, m.p. 106°, 87°, and 124°, respectively. *o*-Amino-benzophenone is produced from tolyl-sulphoanthranil chloride and benzene in the presence of aluminium chloride and hydrolysis of the tolyl-sulphonamino-benzophenone thus produced (*Ullmann*, *Ber.* 35, 4273; 39, 4332), as well as from the amide of *o*-benzoyl-benzoic acid by the action of sodium hypobromite (*Graebe*, *Ber.* 27, 3483; Ann. 291, 8). A mixture of *o*- and *p*-amino-benzophenone in the form of their benzoyl derivatives,  $\text{C}_6\text{H}_5\text{CONHC}_6\text{H}_4\text{COC}_6\text{H}_5$ , is obtained by intra-

molecular migration of atoms from dibenzoyl-aniline,  $(C_6H_5CO)_2NC_6H_5$ , the product first obtained by heating together 2 mols. benzoyl chloride and 1 mol. aniline to  $220^\circ$  (Chattaway, Proc. 19, 57; 20, 60). *o*-Amino-benzophenone oxime, m.p.  $156^\circ$ , isomerises under the influence of hydrochloric acid at high temperatures to *o*-phenylene-benzamidine (Auwers, Ber. 24, 2385). Acetyl-*o*-amino-benzophenone, m.p.  $89^\circ$ . *p*-Dimethylamino-benzophenone, *p*-benzoyl-dimethyl-aniline, m.p.  $90^\circ$ , also obtained by the action of conc. hydrochloric acid on malachite green at  $180^\circ$  (Doebner, Ann. 217, 257; Albrecht, Ber. 21, 3293; Limpricht, Ann. 307, 307), and by the action of heat on *p*-dimethylamino-benzoylbenzoic acid (p. 523). For further derivatives of *p*-amino-benzophenone, see Dinglinger, Ann. 311, 147.

For brominated amino-benzophenones, see Montagne, Rec. 42, 499.

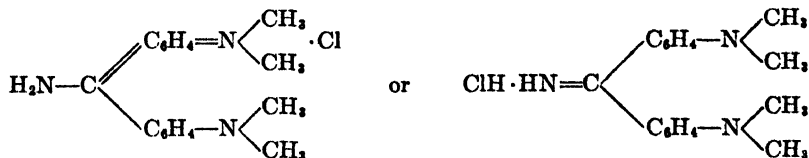
*Ring-formation with o-amino-benzophenone.*—1. If *o*-amino-benzophenone is heated with lead oxide it is converted into acridone (Graebe, Ber. 27, 3484). 2. If *o*-aminobenzophenone is treated with nitrous acid, fluorenone or diphenylene ketone is formed (Graebe, Ber. 27, 3484). 3. *o*-Amino-benzophenone oxime readily gives phenyl-indoxazene with nitrous acid (Zincke, Ber. 26, 1667). 4. *N*-Acetyl-*o*-amino-benzophenone condenses on heating with alcoholic ammonia to  $\alpha$ -phenyl- $\beta$ -methyl-quinazoline (Bischler, Ber. 25, 3082). 5. The oxime gives with acetic anhydride acetyl-phenyl-isoindazole (Auwers, Ber. 24, 2383; 29, 1255). 6. *o*-Amino-benzophenone condenses with acetone and caustic soda to  $\alpha$ -methyl- $\gamma$ -phenyl-quinoline (Geigy, Ber. 18, 2405). 7. *o*-Amino-benzophenone hydrochloride gives anhydro-*ins*-*o*-amino-benzophenone on heating (Sondheimer, Ber. 29, 1272).

**DIAMINO-BENZOPHENONES.** 2,2', 3,3', and 4,4'-diamino-benzophenones, m.p.  $134^\circ$ ,  $173^\circ$ , and  $239^\circ$ , respectively. 2,2'-Diamino-benzophenone gives xanthone and *o*-hydroxy-fluorenone (Staedt, Ber. 28, 111) when treated with nitrous acid. 4,4'-Diamino-benzophenone gives substantive cotton dyes (Wiekellhaus, Ber. 22, 988).

*N,N'*-Tetramethyl-4,4'-diamino-benzophenone (Michler's ketone),  $CO-[C_6H_4[4]N(CH_3)_2]_2$ , m.p.  $173^\circ$ , is formed by the fission of hexamethyl-pararos-aniline (p. 536) by heating with hydrochloric acid (Michler, Ber. 19, 109). It is prepared technically by the action of carbonyl chloride on dimethylaniline in the presence of aluminium chloride. Nitrous acid converts it into nitroso-trimethyl-diamino-benzophenone (Herzberg, Ber. 24, 3198). When treated with dimethylaniline and phosphorus trichloride it gives methyl violet (p. 537), and with phenyl-naphthylamine it gives Victoria blue. Oxime, m.p.  $233^\circ$  (Munchmeyer, Ber. 19, 1852). Phenylhydrazone, m.p.  $174^\circ$  (Möhlau, Ber. 35, 366). The ketone combines with two molecules of dimethyl sulphate to give a bis-quaternary ammonium salt (Zohlen, J. pr. [2], 66, 393).

Tetramethyl-4,4'-diamino-thiobenzophenone,  $CS[C_6H_4[4]N(CH_3)_2]_2$ , m.p.  $202^\circ$ , is produced by the action of thiophosgene,  $CSCl_2$ , on carbon disulphide, or dimethylaniline in the presence of zinc chloride, and of hydrogen sulphide on an alcoholic solution of auramine at  $60^\circ$ . It forms ruby red leaves with a bluish lustre, or a cantharidene green crystalline powder (Graebe, Ber. 20, 3266; V. Meyer, Ber. 20, 3290; Weinmann, Bull. soc. ind. Mulhouse 1898, 40). When heated with alcoholic ammonia under pressure it is converted quantitatively into auramine base.

*N,N'*-Tetramethyl-4,4'-diamino-benzophenone-imide, or auramine base,  $[(CH_3)_2N(C_6H_4)]_2C:NH$ , m.p.  $136^\circ$ , combines with dimethyl sulphate to give the methyl sulphate of methyl-auramine (Zohlen, J. pr. [2] 66, 387). The dye, auramine, is the hydrochloride of auramine base, of which the constitution may be represented by the following formulae:

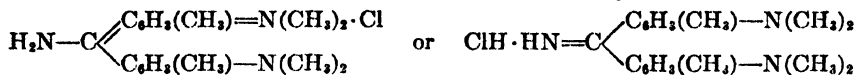


(cf. Semper, Ann. 381, 234; Grandmougin, Ber. 47, 2127). It is formed from tetramethyl-diamino-benzophenone by heating it with ammonium chloride and



zinc chloride, and from *p*-dimethyl-amino-benzamide by the action of dimethyl-aniline and zinc chloride (Ger. Pat. 77,328). Similar dyes are produced with primary amines and diamines (*Fehrmann*, Ber. 20, 2844; Ger. Pats. 77,328 and 108,346). Auramine forms golden-yellow leaflets, and cotton, mordanted with tannin, is dyed a beautiful yellow. With potassium cyanide it gives the nitrile or tetramethyl-diamino-diphenyl-glycocol (*Albrecht*, Ber. 27, 3294).

**N,N'-Tetramethyl-diamino-di-*o*-tolyl-ketone**,  $\text{CO}[\text{C}_6\text{H}_3(\text{CH}_3)\text{N}(\text{CH}_3)_2]_2$ , when heated with ammonium chloride and zinc chloride gives a homologue of auramine, namely the hydrochloride of tetramethyl-diamino-di-*o*-tolyl-imino-methane:



This dye, known as auramine GGG, carbonises at 250° without melting (*Rassow*, J. pr. [2], 85, 497).

**2,3', 2,4', 3,4'-Diamino-benzophenones**, m.p. 80°, 128°, and 131-132°, respectively (*Staedel*, Ann. 283, 149; *Baeyer*, Ann. 354, 179; *Staedel*, Ber. 28, 111).

**Benzophenone-*o*-sulphonic acid**,  $\text{C}_6\text{H}_5\text{COC}_6\text{H}_4[2]\text{SO}_3\text{H}$ , is obtained from *o*-thiobenzoic anhydride by the action of benzene and aluminium chloride (*Kranich*, Ber. 33, 3486).

**Benzophenone-3,3'(?)-disulphonic acid**,  $(\text{SO}_3\text{HC}_6\text{H}_4)_2\text{CO}$ , chloride, m.p. 138° (*Lapworth*, J. 73, 402).

**Hydroxy-benzophenones** are formed: 1. From amino-benzophenones, *o*-amino-benzophenone (p. 518) being converted chiefly into fluorenone. 2. By breaking down xanthenes, which can be regarded as cyclic phenyl ethers of *o,o'*-dihydroxy-benzophenones, by means of caustic alkali. 3. From benzoic acids or hydroxy-benzoic acids and phenols by condensation with zinc chloride or phosphorus oxychloride (*Nencki*, Ber. 26, R 587), sulphuric acid or stannic chloride (Ger. Pats. 49,149 and 50,450/51; *Graebe*, Ber. 24, 967). 4. From phenols, by the action of benzoyl chloride, zinc dust, zinc chloride, or aluminium chloride (*Witt*, Ber. 12, 261). 5. From phenols, or their benzoyl esters by the action of benzotrichloride and zinc oxide (*Doebner*, Ber. 10, 1969). 6. From benzotrichloride and phenols with alkalis (*Herber*, Ber. 24, 3677). 7. From the acid chlorides of phenol-carboxylic acids and their methyl, acetyl, or carbomethoxy-derivatives, by condensation with benzene in the presence of aluminium chloride (*Anschtütz*, Ann. 346, 381; *Fischer*, Ber. 42, 1015). 8. From phenols and nitriles (e.g., benzonitrile) by the action of hydrochloric acid in the presence of zinc chloride. The corresponding ketimide-chloride is first formed, and is then converted into the ketone by boiling with water (*Hoesch*, Ber. 48, 1122; *Houben*, Ber. 59, 2878).

**HYDROXY-BENZOPHENONES WHICH CONTAIN ONLY ONE HYDROXYL GROUP IN A BENZENE NUCLEUS.** *o*-Hydroxy-benzophenone, *o*-benzoyl-phenol, m.p. 41°, is produced, together with phenyl benzoate by method 6. It is also formed by the breakdown of phenyl-indoxazene (*Cohn*, Mo. 17, 102); it is best prepared, however, from *O*-methyl salicylyl chloride by the action of benzene and aluminium chloride (*Ullmann*, Ber. 35, 2811). *o*-Methoxy-benzophenone, m.p. 39°, see *Hoerner*, Ber. 41, 332. *o*-Hydroxy-benzophenone oxime, m.p. 133-134° (*Cohn*, Mo. 17, 109). *o*-Hydroxy-benzophenone anil, m.p. 138°, see p. 516. *m*-Hydroxy-benzophenone, m.p. 116°, prepared by methods 1, 4, 5, and 7 (*Hartmann*, Ber. 25, 3533). *p*-Hydroxy-benzophenone, m.p. 132-133°, prepared by method 8 (*Meyer*, Ber. 56, 98) or by the transformation of phenyl benzoate (*Minajeff*, C. 1927, I, 84). Two oximes of *p*-hydroxy-benzophenone are known, differing as *cis-trans* isomerides about the C=N— double bond. *Syn*-

*p*-Hydroxy-benzophenone oxime,  $\text{C}_6\text{H}_5-\text{C} \begin{array}{l} \diagup \text{C}_6\text{H}_4(\text{OH}) \\ \diagdown \text{N}-\text{OH} \end{array}$ , m.p. 81°, is obtained

from the *anti*-isomeride by heating in alkaline solution for several hours. On fusion, or by the action of hydrochloric acid at ordinary temperature, it is converted into the *anti*-isomeride (*Smith*, Ber. 24, 4040). *Anti-p*-hydroxy-benzo-

phenone oxime,  $\text{C}_6\text{H}_5-\text{C} \begin{array}{l} \diagup \text{C}_6\text{H}_4(\text{OH}) \\ \diagdown \text{HO}-\text{N} \end{array}$ , m.p. 152°. On boiling with sodium hydroxide it is converted into the *syn*-isomeride. *m*- and *p*-Methoxy-benzophe-

none, m.p. 37° and 61°, b.p. 343° and 355°, respectively, are obtained from *m*- and *p*-methoxybenzoyl chloride by the action of benzene and aluminium chloride (Ullmann, Ber. 35, 2813). 2,2'-, 3,3'-, and 4,4'-Dihydroxy-benzophenone, m.p. 173°, 170°, 210°, respectively, and 2,3'- and 2,4'-dihydroxy-benzophenones, m.p. 126° and 151°, respectively, are produced from the corresponding diamino-benzophenones. 2,2'-Dihydroxy-benzophenone is also formed from its anhydride, xanthone, or diphenylene-ketone oxide, by careful fusion with caustic potash (Graebe, Ber. 19, 2809). 2,4'-, and 4,4'-Dihydroxy-benzophenone are formed by the condensation of salicylic acid and phenol with stannic chloride (Baeyer, Ann. 354, 177). 4,4'-Dihydroxy-benzophenone is produced in the decomposition of aurin, benzaurin, phenolphthalein, and rosaniline on heating with water or caustic potash (Liebmann, Ber. 16, 1931). 3,4'-Dihydroxy-benzophenone, m.p. 206°, is obtained from the diamino-compound. For methyl-substituted hydroxy-benzophenones, see Meisenheimer, J. pr. [2] 119, 315.

**HYDROXY-BENZOPHENONES WHICH CONTAIN MORE THAN ONE HYDROXYL GROUP IN A BENZENE RING** are prepared by method 3, but particularly by method 8. The ketones obtained from pyrogallol, or gallic acid are important, as, like alizarin, they are mordant dyes (Noellting, Ber. 30, 2590). The dye, alizarin yellow A,  $(\text{HO})_2[2,3,4]\text{C}_6\text{H}_2\text{COC}_6\text{H}_5$ , obtained from benzoic acid and pyrogallol, has m.p. 140° (Graebe, Ann. 269, 275; Ber. 32, 1686). Isomeric with the latter is 3,4,5-trihydroxy-benzophenone, m.p. 176°, which is obtained from tricarbomethoxy-galloyl chloride,  $(\text{CH}_3\text{OOCO})_3\cdot\text{C}_6\text{H}_2\cdot\text{COCl}$ , benzene, and aluminium chloride (Fischer, Ber. 42, 1015).

2,5-Dihydroxy-benzophenone,  $\text{C}_6\text{H}_3\text{COC}_6\text{H}_3[2,5](\text{OH})_2$ , m.p. 125°, is formed from benzaldehyde and quinone in sunlight (Klinger, Ber. 24, 1340; Herzog, Ber. 41, 143; p. 235). 2,4-Dihydroxy-benzophenone, m.p. 144°, has been obtained by the action of ethyl benzoate on resorcinol (Sen, J. Indian Chem. Soc. 6, 557). 2,4,2',4'-Tetrahydroxy-benzophenone,  $[(\text{OH})_2\text{C}_6\text{H}_3]_2\text{CO}$ , is obtained by the fusion of fluorescein chloride (p. 548) with caustic soda. On heating it is converted into dihydroxy-xanthone (Meyer, Ber. 32, 2103). 2,5,2',5'-Tetramethoxy-benzophenone, m.p. 109°, is obtained from iodohydroquinone-dimethyl ether, magnesium, and carbon dioxide (Kauffmann, Ber. 41, 4423). Further polyhydroxy-benzophenones which have been prepared in large numbers, especially by method 8, see Stephen, J. 117, 1529; Shoesmith, J. 125, 113; Atkinson, J. 1926, 2688; Bogert, Am. 52, 837.

A series of hydroxy-benzophenone derivatives have been obtained from cotobark and paracoto-bark, from certain Bolivian trees. These are of medicinal value. Cotoin,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_2[2,6](\text{OH})_2[4]\text{OCH}_3$ , m.p. 129°; hydrocotoin,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_2[6](\text{OH})_2[4](\text{OCH}_3)_2$ , m.p. 97°; methyl-hydrocotoin,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_2[2,4,6](\text{OCH}_3)_3$ , m.p. 113° (Clamician, Ber. 25, 1119; 26, 2340; 27, 419); proto-cotoin,  $[2,4](\text{CH}_3\text{O})_2\cdot[6](\text{OH}\cdot\text{C}_6\text{H}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3[3,4]\text{O}_2\text{CH}_3)$ , m.p. 141°; methyl-protocotoin, the methyl ether of protocotoin. Cotogenin,  $[2,4,6](\text{OCH}_3)_3\cdot\text{C}_6\text{H}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3[3,4](\text{OH})_2$ , m.p. 219-220°, and iso-protocotoin,  $[2,6](\text{OCH}_3)_2[4](\text{OH}\cdot\text{C}_6\text{H}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_3[3,4]\text{O}_2\text{CH}_3)$ , m.p. 165-166°, have also been isolated. The synthesis of these substances has been carried out, and they are prepared artificially usually by method 8 (Späth, Mo. 42, 267; 49, 229, 429; Karrer, Helv. 11, 789; Houben, J. pr. [2], 123, 89).

Closely related to these substances is maclurin,  $(\text{OH})_2[3,4]\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2[2,4,6](\text{OH})_2$  (Kostanecki, Ber. 39, 4014), which is decomposed when heated with concentrated potash into protocatechuic acid and phloroglucinol, and has been synthesised from protocatechuic nitrile and phloroglucinol (Hoesch, Ber. 50, 462), and also aromadendrin, which appears to have the constitution  $(\text{OH})[4]\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_2[2,4,6](\text{OH})_2$  (Nishikawa, J. 121, 839).

The pentamethyl ether of maclurin, obtained by methylating the latter with dimethyl sulphate, has m.p. 157°, and has been obtained synthetically from veratroyl chloride, phloroglucinol trimethyl ether and aluminium chloride (Kostanecki, Ber. 39, 4022).

#### (d) Carboxylic Acids of the Diphenylmethane Group

These carboxylic acids fall into three groups: A. Diphenylmethane carboxylic acids. B. Diphenyl-carbinol carboxylic acids. C. Benzophenone carboxylic acids.

## A. Diphenylmethane Carboxylic Acids

*o*-, *m*-, and *p*-Benzyl-benzoic acids,  $C_6H_5 \cdot CH_2 \cdot C_6H_4COOH$ , m.p. 117°, 107°, and 155–156°, respectively. The ortho-acid gives anthranol (p. 651) when warmed with sulphuric acid (Zincke, Ber. 9, 633; Cassirer, Ber. 25, 3022; Fischer, Ber. 27, 2789; Ullmann, Ann. 291, 17). *o*-Cyanodiphenylmethane, m.p. 19°, b.p. 313°, is obtained from *o*-cyanobenzyl chloride by the action of benzene and aluminium chloride. It can also be obtained from *o*-amino-diphenylmethane.

Benzyl-iso- and -terephthalic acids,  $C_6H_5 \cdot CH_2 \cdot C_6H_4(COOH)_2$ , see Zincke, Ber. 9, 1765.

Diphenylmethane-2,2'-dicarboxylic acid,  $CH_2(C_6H_4[2]COOH)_2$ , m.p. 254°, is obtained by the reduction of the lactone of diphenyl-carbinol-2,2'-dicarboxylic acid, and in small quantities by the reduction of the dilactone of benzophenone-2,2'-dicarboxylic acid. It is converted into anthranol-carboxylic acid by conc. sulphuric acid (Graebe, Ann. 242, 253). Diphenylmethane-3,3'-dicarboxylic acid, m.p. 220–225°. Diphenylmethane-4,4'-dicarboxylic acid, m.p. 334–336° (Schöpf, Ber. 27, 2324; Liebermann, Ber. 45, 1186). Diphenylmethane-2,4'-dicarboxylic acid, m.p. 220°, gives benzophenone-2,4'-dicarboxylic acid on oxidation with permanganate. When allowed to stand with conc. sulphuric acid, anthranol-(9)-carboxylic acid-(2) is formed (Limpricht, Ann. 309, 115).

Methylene-digallic acid,  $CH_2[C_6H(OH)_3COOH]_2$ , see Mohlau (Ber. 31, 259).

## B. Diphenyl-carbinol Carboxylic Acids

✓ Diphenyl-carbinol *o*-carboxylic acid lactone, phenyl-phthalide,  $C_6H_4 \begin{matrix} \swarrow [1]CHC_6H_5 \\ \searrow [2]COO \end{matrix}$ ,

m.p. 115°, is obtained by the reduction of *o*-benzoylbenzoic acid, and the decomposition of diphenyl-carbinol-*o,o'*-dicarboxylic acid by heating. The acid corresponding to the lactone melts at 50°, and is very unstable (Cornillot, Ann. chim. [10], 8, 120), but its salts and esters are known. The lactone is converted into anthraquinone by the action of phosphorus pentachloride (Graebe, Ber. 21, 1315). *o*-Cyanobenzhydrol,  $C_6H_5CH(OH)C_6H_4[2]CN$ , is obtained from *o*-cyanodiphenyl-chloromethane,  $C_6H_5CHCl \cdot C_6H_4CN$ , the product of interaction of chlorine and cyano-diphenylmethane (Gabriel, Ber. 29, 1315). *m*- and *p*-Benzhydryl-benzoic acid, m.p. 121° and 164°, respectively (Serff, Ann. 220, 242). *p*-Tolyl-phthalide, m.p. 129°, and homologues, see Gresly, Ann. 234, 233. Hy-

droxy-phenyl-phthalide,  $C_6H_4 \begin{matrix} \swarrow CHC_6H_4OH \\ \searrow COO \end{matrix}$ , m.p. 180°, is obtained from phthalaldehydic acid (p. 379), phenol and sulphuric acid (73%) (Bistrzycki, Ber. 27, 2362; 31, 2790).

Benzhydrol-*o,o'*-dicarboxylic acid lactone,  $C_6H_4 \begin{matrix} \swarrow CH-C_6H_4COOH \\ \searrow COO \end{matrix}$ , m.p. 202°,

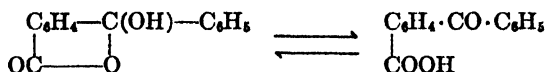
is obtained from the lactone of benzhydrol-tricarboxylic acid,  $(HOOC \cdot C_6H_4)_2 \cdot C(OH)COOH$ , the product of interaction of alkalis and benzil-*o,o'*-dicarboxylic acid (p. 570) on warming (Graebe, Ann. 242, 233).

## C. Benzophenone Carboxylic Acids

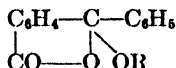
These are formed (1) by oxidation of alkyl-diphenylmethanes, alkyl-benzophenones, diphenylmethane-carboxylic acids, and benzhydrol-carboxylic acids; (2) from benzoyl chloride, benzoic anhydride, and zinc chloride (Doebner, Ber. 14, 647); (3) from phthalic anhydride, benzene, and aluminium chloride (Haller, Ber. 41, 3627).

*o*-Benzoyl-benzoic acid,  $C_6H_5 \cdot CO \cdot C_6H_4[2]COOH + H_2O$ , m.p. 127° (anhydrous), is produced by the oxidation of *o*-tolyl-phenylmethane, *o*-methyl-benzophenone, *o*-benzyl- and *o*-benzhydryl-benzoic acids. It is prepared by method (3). On heating with phosphorus pentoxide it is converted into anthraquinone, and on distillation with zinc dust it gives anthracene. With benzene and aluminium chloride it forms diphenyl-phthalide (p. 544), and with phenol and stannic chloride, phenyl-phenol-phthalide (p. 545).

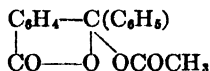
*o*-Benzoyl-benzoic acid, its ester and chloride occur in two structural isomeric forms, which are in tautomeric equilibrium. The two forms are the keto- and hydroxy-lactone forms:



The keto-form is coloured yellow, the hydroxy-lactone is colourless (*Hantzsch*, Ber. 49, 213). The normal esters, which are derived from the keto-form, are prepared by treating the acid with alcohol, or by means of the silver salt. The *pseudo*-esters of the formula:



are obtained through the *pseudo*-chloride, prepared by distilling the acid with thionyl chloride (*Egerer*, Mo. 34, 69). When benzoyl-benzoic acid is warmed with acetic anhydride it reacts in the hydroxy-lactone form and gives **acetyl-benzoyl-benzoic acid**:



(*Pechmann*, Ber. 14, 1865). This compound melts at 117°. The same type of tautomerism is also found in the derivatives of *o*-benzoyl-benzoic acid (*Perard*, Ann. chim. [9], 7, 370; 8, 22).

**Oxime-anhydride**, m.p. 162°, obtained from benzoyl-benzoic acid and hydroxylamine hydrochloride, gives phthalanil on heating to 130° (*Thorpe*, Ber. 26, 1262, 1795). For the constitution of the oxime and its behaviour when submitted to the Beckmann transformation, see *Meisenheimer*, Ber. 57, 289. **Phenyl-lactazam**,  $\text{C}_6\text{H}_5\left\langle \begin{array}{l} [1]\text{C}(\text{C}_6\text{H}_5):\text{N} \\ [2]\text{CO}-\text{O}-\text{NC}_6\text{H}_5 \end{array} \right\rangle$ , m.p. 181° (*Roser*, Ber. 18, 805).

A large number of **chloro-benzoyl-benzoic acids** have been prepared from chlorinated phthalic anhydrides by reaction with benzene or its chloro-substitution products in the presence of aluminium chloride (*Graebe*, Ann. 238, 338). Homologous **methyl-benzoyl-benzoic acids** are prepared from phthalic anhydride and toluene, and other methyl-benzenes (*Gresly*, Ann. 234, 241; *Limpricht*, Ann. 311, 178). Phthalic anhydride and dimethylaniline give dimethylamino-benzoyl-benzoic acid, **dimethylaniline-phthaloyl acid**,  $\text{C}_6\text{H}_5(\text{COOH})\text{COC}_6\text{H}_4\text{N}(\text{CH}_3)_2$ , m.p. 205° (*Limpricht*, Ann. 307, 305). For transformation and substitution products of this acid see *Haller*, Bull. [3], 25, 165; C.r. 132, 746. The substituted benzoyl-benzoic acids yield on warming with conc. sulphuric acid, the corresponding substituted anthraquinones (*Hofmann*, Mo. 36, 805).

***m*-Benzoyl-benzoic acid**,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4[3]\text{COOH}$ , m.p. 161°, is obtained from isophthalic chloride, benzene, and aluminium chloride (*Senff*, Ann. 220, 236; *Ador*, Ber. 13, 320). ***p*-Benzoyl-benzoic acid**, m.p. 194°, is prepared by method (1) (*Meyer*, Mo. 28, 1224).

**Benzophenone-2,2'-dicarboxylic acid**,  $\text{CO}(\text{C}_6\text{H}_4[2]\text{COOH})_2$ , melts in the range 150°–200°, with transformation into its dilactone, which is actually derived from the tautomeric form of benzoyl-benzoic acid (see above). It is produced by the oxidation of benzhydrol-2,2'-dicarboxylic acid lactone with permanganate.

**Benzophenone-dicarboxylic dilactone**,  $\begin{array}{ccc} \text{COO} & & \text{OCO} \\ & \diagdown \quad \diagup & \\ \text{C}_6\text{H}_4 & -\text{C}- & \text{C}_6\text{H}_4 \end{array}$ , m.p. 212°, is ob-

tained by boiling the aqueous solution of the acid and warming the alcoholic solution with hydrochloric acid (*Graebe*, Ann. 242, 246). **2,4'- and 4,4'-benzophenone-dicarboxylic acid**, m.p. 235°, and over 360°, respectively (*Limpricht*, Ann. 309, 98; 312, 96). **Phthaloyl-salicylic acid**,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{COC}_6\text{H}_4(\text{OH})\cdot\text{COOH}$ , m.p. 244°, is produced from methyl salicylate, phthaloyl chloride, and aluminium chloride (*Limpricht*, Ann. 303, 280).

**Benzoyl-phthalic acid**,  $C_6H_5 \cdot CO \cdot C_6H_4[2,3](COOH)_2$ , m.p.  $183^\circ$ , with anhydride formation, is obtained from hemimellitic anhydride, benzene, and aluminium chloride (*Graebe*, Ann. 290, 217). It gives anthraquinone-carboxylic acid with conc. sulphuric acid. **1,3,4-Benzoyl-phthalic acid**, m.p.  $189^\circ$ , is obtained by the oxidation of *o*-xyloyl-benzoic acid (*Limpricht*, Ann. 312, 99). **Benzophenone-2,3,4'-tricarboxylic acid (phthaloyl-phthalic acid)** is obtained by oxidation of 4'-methyl-diphenylketone-2,3'-dicarboxylic acid; m.p.  $199.5^\circ$  (*de Diesbach*, Helv. 7, 618). **Benzophenone-2,4,2',4'-tetracarboxylic acid** is obtained by oxidation of di-*m*-xylyl-ketone. On treatment with hydrochloric acid it is converted into its dilactone, which has been resolved into its optical antipodes (*Mills*, J. 119, 2094).

**Hydroxybenzoyl-benzoic acids** are produced from phenols and phthalic anhydride in acetylene tetrachloride by the aid of aluminium chloride (*Ullmann*, Ber. 52, 2098). With resorcinol this reaction occurs at  $126^\circ$  without a catalyst (*Orndorff*, Am. 46, 2276). For the ester, salts, and substitution products of *p*-hydroxy-benzoyl-*o*-benzoic acid, see *Kelly*, Am. 44, 1518.

**BENZYL-DIPHENYLS**,  $C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot C_6H_5$ , are produced from diphenyl, benzyl chloride, and zinc dust. ***p*-Benzyl-diphenyl**, m.p.  $85^\circ$ , b.p.  $285^\circ$  (100 mm.). **Isobenzyl-diphenyl**, m.p.  $54^\circ$ , b.p.  $283-287^\circ$  (110 mm.) (*Goldschmidt*, Mo. 2, 432).

***p*-Phenylbenzyl-*o*-benzoic acid**,  $C_6H_5[4]C_6H_4[1]CH_2[2']C_6H_4[1']COOH$ , m.p.  $184^\circ$ , and ***p*-phenylbenzyl- $\alpha$ -hydroxy-*o*-benzoic acid**,  $C_6H_5[4]C_6H_4[1]CH(OH)[2']C_6H_4[1']COOH$ , m.p.  $204^\circ$ , are obtained by the reduction of *p*-phenylbenzoyl-*o*-benzoic acid,  $C_6H_5[4]C_6H_4[1]CO[2'] \cdot C_6H_4[1']COOH$ , m.p.  $225^\circ$ , which is itself obtained by the action of aluminium chloride on a solution of diphenyl and phthalic anhydride in ligroin (*Kaiser*, Ann. 257, 96; *Elbs*, J. pr. [2], 41, 149).

**DIBENZYL-BENZENES**. A second benzyl radical can be introduced into benzene and its homologues by reactions similar to those by which the first was introduced, i.e., (1) by the action of zinc dust (*Zincke*, Ber. 9, 31), or aluminium chloride on a solution of benzyl chloride in the hydrocarbons, and (2) by the action of sulphuric acid on a mixture of benzene and acetaldehyde or formaldehyde (*Baeyer*, Ber. 6, 221; *Thiele*, Ber. 37, 1467). **1,4- and 1,2-( $\alpha$ - and  $\beta$ -)Dibenzyl-benzene, triphenyl-dimethane**, m.p.  $86^\circ$  and  $78^\circ$ , respectively. ***p*-Dimethyl-triphenyl-dimethane**,  $CH_3 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot CH_3$ , is obtained from *p*-xylylene bromide in toluene by the action of zinc bromide, m.p.  $83.5^\circ$ ; it can also be readily obtained by the reduction of di-*p*-toluyl-benzene,  $CH_3 \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot CH_3$ , m.p.  $194^\circ$ . For further derivatives see *Cammerade*, Bull. Belge. 40, 144. **bis-Amino-benzyl-resorcinol**,  $(NH_2C_6H_4 \cdot CH_2)_2 \cdot C_6H_2(OH)_2$ , m.p.  $213^\circ$ , is obtained as a by-product in the condensation of *p*-aminobenzyl alcohol with resorcinol by means of hot dilute sulphuric acid (*Friedländer*, Mo. 23, 973).

***o*-Dibenzhydrylbenzene**,  $C_6H_4(CHOHC_6H_5)_2$ , m.p.  $120^\circ$ , is obtained by reduction of *o*-dibenzoylbenzene (see below) with sodium amalgam; when acted upon by mineral acids, it is readily converted into *sym*-diphenylphthalane,

$C_6H_5 \begin{array}{c} \diagup CH-C_6H_5 \\ > O \\ \diagdown CH-C_6H_5 \end{array}$ , m.p.  $96^\circ$ , with loss of water. This compound can also be obtained synthetically by the action of phenyl magnesium bromide on phenylphthalide (p. 522), followed by elimination of water from, and reduction of the product (*Guyot*, C.r. 140, 1348).

***o*-, *m*-, and *p*-Dibenzoylbenzenes, phenylene-diphenyl ketone, phthalophenone**,  $C_6H_4(COC_6H_5)_2$ , m.p.  $148^\circ$ ,  $100^\circ$ , and  $160^\circ$ , respectively. The *o*- and *p*-compounds are obtained by the oxidation of the corresponding dibenzylbenzenes. The *m*- and *p*-compounds are obtained from *m*- and *p*-phthaloyl chlorides, benzene, and aluminium chloride (*Ador*, Ber. 13, 320); *as-o*-phthaloyl chloride gives diphenyl-phthalide under these conditions (*Noelting*, Ber. 19, 146; *Munchnmeyer*, Ber. 19, 154). ***o*-Dibenzoylbenzene** is tautomeric with diphenylphthalide (*Tasman*, Rec. 46, 653). **1-Amino-2,4-dibenzoyl-benzene**,  $C_6H_3[1]NH_2[2,4](COC_6H_5)_2$ , m.p.  $138^\circ$ , is obtained in the form of its benzoyl compound, m.p.  $156^\circ$ , by heating 1 mol. of aniline with 3 mols. of benzoyl chloride, when the dibenzoylaminobenzophenone (see p. 519) first formed undergoes intramolecular rearrangement (*Chatlaway*, Proc. 20, 223; J. 85, 1663).

**Dibenzoyl-mesitylene**,  $(\text{CH}_3)_3[1,3,5]\text{C}_6\text{H}(\text{COC}_6\text{H}_5)_2$ , m.p.  $117^\circ$ , is obtained from mesitylene, 2 mols. of benzoyl chloride, and aluminium chloride. When oxidised it gives *sym*- and *as*-dibenzoyl-mesitylenic acid,  $(\text{C}_6\text{H}_5\text{CO})_2\text{C}_6\text{H}(\text{CH}_3)_3\text{COOH}$ , m.p.  $222^\circ$  and  $174^\circ$ , respectively, *sym*- and *as*-dibenzoyl-uvitic acid,  $(\text{C}_6\text{H}_5\text{CO})_2\text{C}_6\text{H}(\text{CH}_3)(\text{COOH})_2$ , m.p.  $262^\circ$  and  $211^\circ$ , respectively, and finally dibenzoyl-trimesic acid,  $(\text{C}_6\text{H}_5\text{CO})_2\text{C}_6\text{H}(\text{COOH})_3$ , m.p.  $250^\circ$  (*Mills*, J. 81, 1311).

## 2. TRIPHENYLMETHANE GROUP

Triphenylmethane, tolyldiphenylmethane, and ditolylphenylmethane are the parent substances of the rosaniline dyes, malachite greens, aurines, and phthaleins.

### (a) Hydrocarbons

The general methods of preparation of the triphenylmethane hydrocarbons follow from the methods available for the preparation of triphenylmethane itself.

**Triphenylmethane**,  $\text{CH}(\text{C}_6\text{H}_5)_3$ , b.p.  $92^\circ$ , b.p.  $358^\circ$ , is prepared:

1. By the action of benzal chloride on mercury diphenyl (*Kekulé*, *Franchimont*, Ber. 5, 907).

2. By the action of (a) zinc dust, or (b) aluminium chloride on a mixture of benzene and either benzal chloride or benzotrichloride (*Böttiger*, Ber. 12, 976; *Doebner*, Ber. 12, 1468; *Schwarz*, Ber. 14, 1526).

3. By the action of chloroform or carbon tetrachloride on benzene in the presence of aluminium chloride (*Fischer*, Ann. 194, 254; *Allen*, Ann. 227, 107; *Kölliker*, Ann. 228, 254; cf. *Morris*, Am. 26, 499).

4. By the action of phenyl magnesium bromide on chloroform or benzal chloride (*Reychler*, Belge [3], 35, 737).

5. By the action of phosphorus pentoxide on a mixture of diphenylcarbinol and benzene at  $140^\circ$  (*Hemilian*, Ber. 7, 1204).

6. By reduction of triphenylcarbinol or triphenyl-bromomethane (p. 529) (*Acree*, Ber. 37, 616; *Bistrzycki*, Ber. 37, 1249; *Tshitshibabin*, Ber. 44, 441).

7. By the action of nitrous acid and alcohol on di- and tri-amino-triphenylmethane sulphate (*Fischer*, Ann. 206, 152). This reaction is of importance in demonstrating the connection between pararosaniline and triphenylmethane.

Triphenylmethane crystallises from benzene with 1 mol. of benzene of crystallisation. This compound melts at  $75^\circ$ . It also separates from solution in thiophene, pyrrole, and aniline with 1 mol. of the solvent (*Liebermann*, Ber. 26, 853; *Hartley*, J. 89, 1013). Two polymorphic forms of the substance, of which only one is stable, can be crystallised from solution in alcohol. When oxidised it is converted into triphenylcarbinol, and when reduced by hydrogen and finely divided nickel at  $220^\circ$ , it gives **tricyclohexylmethane**, b.p.  $140^\circ$  (20 mm.) (*Godchot*, C.r. 147, 1057). When heated with hydrogen iodide and red phosphorus to  $280^\circ$ , it is decomposed into benzene and toluene. When heated with potassium, potassium-triphenylmethane,  $(\text{C}_6\text{H}_5)_3\text{CK}$ , is formed (see p. 170). This compound combines with carbon dioxide to give potassium triphenylacetate (p. 557). For the alkali-metal salts of triphenylmethane, see *Hantzsch*, Ber. 54, 2620.

*o*-, *m*-, and *p*-Methyltriphenylmethane, diphenyl-*o*-, *m*-, *p*-tolylmethane,  $(C_6H_5)_2CH \cdot C_6H_4CH_3$ , m.p. 83°, 62°, and 71°, respectively, are obtained by the reduction of the corresponding carbinols. The *m*-compound is obtained by the action of nitrous acid and alcohol on leucaniline sulphate (*Fischer*, Ann. 194, 282; cf. *Bistrzycki*, Ber. 37, 1245). *p*-Tolylidiphenylmethane can be readily obtained from diphenyl-carbinol (p. 512), toluene, and stannic chloride (*Bistrzycki*, Ber. 37, 659). Diphenyl-*o*-, *m*-, and *p*-xylylmethanes, m.p. 68°, 61°, and 92°, respectively, are obtained by the action of phosphorus pentoxide on a mixture of diphenylcarbinol and the respective xylene (*Hemilian*, Ber. 16, 2360).

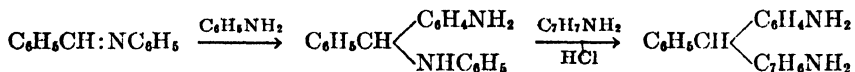
**NITRO-SUBSTITUTION PRODUCTS.** *m*- and *p*-Nitro-triphenylmethane,  $NO_2 \cdot C_6H_4 \cdot CH(C_6H_5)_2$ , m.p. 90° and 93°, respectively, are obtained by the action of zinc chloride on a mixture of benzene and *m*- or *p*-nitrobenzaldehyde (*Tschacher*, Ber. 21, 188; *Baeyer*, Ber. 23, 1622).

*p*-, *p'*-, *p''*-Trinitro-triphenylmethane,  $CH(C_6H_4[4]NO_2)_3$ , m.p. 206°, is obtained by the action of nitric acid on triphenylmethane. It gives, like tetranitrodiphenylmethane (p. 511), an intensely violet sodium salt when treated with sodium ethylate, and it dissolves in alcoholic potash giving a violet solution (*Richter*, Ber. 21, 2476). On further nitration with a mixture of conc. nitric and sulphuric acids, *o*-, *o'*-, *o''*-, *p*-, *p'*-, *p''*-hexanitro-triphenylmethane,  $CH[C_6H_3(NO_2)_2]_3$ , m.p. 260° (decomp.), is formed. When this compound is reduced with alcoholic ammonium sulphide, it gives trinitrotriamino-triphenylmethane (*Baeyer*, Ber. 36, 2779).

*p*-, *p'*-, *p''*-Trinitrodiphenyl-*m*-tolyl-methane,  $(NO_2[4]C_6H_4)_2CH \cdot C_6H_4[4]NO_2[3]CH_3$  (*Fischer*, Ann. 194, 284; *Bistrzycki*, Ber. 37, 1251).

### (b) Amino-compounds

These compounds are produced: 1. By the reduction of the corresponding nitro-compounds. 2. By reduction of the corresponding amino-carbinols, the colour bases of the malachite green and rosaniline group. They are often known as the leuco-compounds corresponding to these dyes. 3. By condensation of diphenyl-carbinol or benzaldehyde with aniline hydrochloride or dimethylaniline hydrochloride in the presence of phosphorus pentoxide or zinc chloride. 4. Mixed diamino-triphenylmethanes may be obtained by the following method: benzyldiene-aniline combines with anilines to give aminobenzhydryl-phenylamines. When these are treated with salts of aromatic amines, they give diamino-triphenylmethanes (Ger. Pat. 111,041):



When the salts of these amino-compounds are oxidised with chloranil or lead dioxide and hydrochloric acid, *etc.*, they are converted into the salts of the colour bases, to which malachite green and rosaniline belong, being derived from triphenyl-carbinol.

*o*-Amino-triphenylmethane,  $(C_6H_5)_2CHC_6H_4[2]NH_2$ , m.p. 129°, is obtained from the corresponding amino-carbinol by reduction with zinc dust and glacial acetic acid (*Baeyer*, Ber. 37, 3198).

*m*-Amino-triphenylmethane, m.p. 120°, is obtained from *m*-nitro-triphenylmethane (*Tschacher*, Ber. 21, 189).

*p*-Amino-triphenylmethane, m.p. 84°, b.p. 248° (12 mm.) (*Baeyer*, Ber. 37, 599). This compound is produced: 1. from *p*-nitro-triphenylmethane; 2. from diphenyl-carbinol, aniline hydrochloride and zinc chloride (*Fischer*, Ann. 206, 155); 3. from phenylbenzhydrylamine,  $(C_6H_5)_2CHNHC_6H_5$  (p. 513) by heating with aniline hydrochloride (*Busch*, Ber. 38, 1768). *p*-Dimethylamino-triphenylmethane,  $(C_6H_5)_2CH \cdot C_6H_4[4]N(CH_3)_2$ , m.p. 132°, is obtained from benzophenone chloride and dimethyl-aniline, from diphenyl-carbinol and dimethylaniline in the presence of phosphorus pentoxide (*Fischer*, Ann. 206, 113), and from benzophenone, dimethylaniline, and zinc chloride (*Doebner*, Ann. 242, 341). *p*-Acetaminotriphenylmethane, m.p. 167°, see *Baeyer*, Ber. 37, 599.

*p*-, *p'*-Diaminotriphenylmethane,  $C_6H_5 \cdot CH(C_6H_4[4]NH_2)_2$ , m.p. 139°, with 1 mol. benzene of crystallisation, m.p. 106°, is the parent base of leuco-malachite green. It is obtained 1. from benzalchloride and aniline by the action of zinc dust; 2. by the action of zinc chloride at 120° on a mixture of benzaldehyde and

aniline hydrochloride (*Fischer*, Ber. 15, 676), or by boiling the mixture with hydrochloric acid (*Mazzara*, Gazz. 15, 50; *Baeyer*, Ber. 37, 2860); 3. by reduction of diaminotriphenyl-chloromethane with zinc dust (*Fischer*, Ber. 15, 676; *Weil*, Ber. 61, 1294). The base forms molecular compounds with benzene and organic bases. The diacetyl derivative, m.p. 240–241°, is difficultly soluble.

For chloro-, nitro-, and hydroxy-diamino-triphenylmethanes, and their molecular compounds, see *Weil*, Ber. 61, 1294.

*p,p'*-**Tetramethyl-diamino-triphenylmethane**, **leuco-malachite green**,  $C_6H_5 \cdot CH[C_6H_4[4]N(CH_3)_2]_2$ , is dimorphous, and crystallises in leaflets, m.p. 93–94°, or in needles, m.p. 102°. The lower melting point substance is obtained by crystallisation from alcohol, the other by crystallisation from benzene. It is obtained by methylation of *p,p'*-diamino-triphenylmethane, and also by the action of benzal chloride on dimethylaniline. It is produced technically by the condensation of benzaldehyde and dimethylaniline with hydrochloric acid or sulphuric acid (also formerly zinc chloride, or oxalic acid) as condensing agent. When oxidised it gives *p,p'*-tetramethyl-diamino-triphenylcarbinol, the base of malachite green.

**Dimethyl-dicyano-diamino-triphenylmethane**,  $[CH_3N(CN)C_6H_4]_2CHC_6H_5$ , m.p. 163°, is obtained from leuco-malachite green by warming it with cyanogen bromide. When hydrolysed with hydrochloric acid this substance gives rise to *p,p'*-dimethyl-diamino-triphenylmethane,  $(CH_3NH \cdot C_6H_4)_2CHC_6H_5$ , m.p. 104° (*von Braun*, Ber. 37, 637).

*o*- and *m*-Nitro-*p,p'*-diamino-triphenylmethane are obtained by the condensation of *o*- and *m*-nitrobenzaldehyde with aniline sulphate in the presence of zinc chloride. The *m*-compound melts at 136° (*Fischer*, Ber. 13, 671; *Renouf*, Ber. 16, 1305).

Just as benzaldehyde and the nitrobenzaldehydes condense with aniline and dimethylaniline, they also condense with *o*- and *p*-toluidine (*Ullmann*, Ber. 18, 2094). *m*-Toluidine and *m*-derivatives of aniline only react readily if the amino-group is methylated (*Kock*, Ber. 20, 1563).

**Triamino-triphenylmethane** is obtained by the reduction of nitro- and nitroamino-triphenylmethanes and the triamino-triphenylcarbinols. The latter form the rosaniline bases if the three amino-groups are in the *p*-position to the C(OH) group, and their reduction products are called leuco-anilines. These exist as white precipitates and are converted into the carbinols by oxidation: *o,p,p'*-triamino-triphenylmethane, or ortholeuco-aniline and *m,p,p'*-triamino-triphenylmethane, or *pseudo*-leuco-aniline, and *p,p',p''*-triamino-triphenylmethane, or *p*-leuco-aniline, gives dyes when oxidised. The *o*-compound gives a brown dye, the *m*-compound a violet dye, and the *p*-compound gives **pararosaniline** (p. 534). *p,p',p''*-Triamino-triphenylmethane can also be obtained by the condensation of *p*-aminobenzaldehyde with aniline in the presence of zinc chloride. Its *tris*-diazonium chloride,  $CH(C_6H_4 \cdot N_2 \cdot Cl)_3$ , gives triphenylmethane when boiled with alcohol.

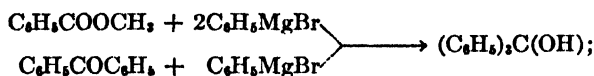
*p,p',p''*-**Triamino-diphenyl-*m*-tolylmethane**, **leuco-aniline**,  $[(NH_2)[4]C_6H_4]_2CH-C_6H_4[4]NH_2[3]CH_3$ , is the leuco-compound corresponding to rosaniline. It is obtained by reduction of the corresponding trinitro-compound; or from the fuchsin salts by heating with ammonium sulphide to 120°, or with zinc dust and hydrochloric acid. The diazonium sulphate is converted into diphenyl-*m*-tolylmethane when boiled with alcohol.



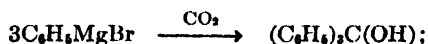
## (c) Carbinols

These compounds are obtained (1) by the oxidation of triphenylmethane hydrocarbons, or their nitro-, or amino-compounds, and can be prepared synthetically by several methods.

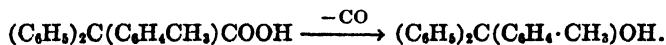
(2) From aryl magnesium halides (a) with aromatic esters or benzophenones (*Baeyer*, Ber. 35, 2024; *Ullmann*, Ber. 36, 406; *Bistrzycki*, Ber. 37, 663; *Acree*, Ber. 37, 990):



(b) by the action of  $\text{CO}_2$ ,  $\text{COS}$ ,  $\text{COCl}_2$ ,  $\text{ClCOOR}$  (*Weigert*, Ber. 36, 1010; *Schroeter*, *ibid.*, 3005; *Houben*, *ibid.*, 3087; *Auwers*, *ibid.*, 3236). Other products are also formed:



(c) from triarylacetic acids (p. 557) by treatment with conc. sulphuric acid, when  $\text{CO}$  is split off (*Geipert*, Ber. 37, 655):



**Triphenylcarbinol**,  $(\text{C}_6\text{H}_5)_3\text{C}(\text{OH})$ , m.p.  $163^\circ$ , b.p. above  $360^\circ$ . *o*-, *m*-, and *p*-Tolyl-diphenylcarbinols,  $(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\cdot\text{CH}_3)\text{C}\cdot\text{OH}$ , m.p.  $98^\circ$ ,  $65^\circ$ , and  $74^\circ$  (*Bistrzycki*, Ber. 37, 656, 1245; *Acree*, *ibid.*, 992). Tri-*p*-tolylcarbinol,  $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{C}\cdot\text{OH}$ , m.p.  $96^\circ$  (*Mothwurf*, Ber. 37, 3153).

Diphenyl-monobiphenyl-carbinol,  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$ , m.p.  $136^\circ$ ; phenyl-dibiphenyl-carbinol,  $(\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4)_2\text{C}(\text{OH})\text{C}_6\text{H}_5$ , m.p.  $151^\circ$ ; tribiphenyl-carbinol,  $(\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4)_3\text{C}\cdot\text{OH}$ , m.p.  $208^\circ$ , see *Schlenk*, Ann. 368, 298.

The OH-group in triphenylcarbinol and its homologues is very reactive. Triphenylcarbinol is very readily converted into ethers by the action of alcohols; triphenylcarbinol-methyl ether,  $(\text{C}_6\text{H}_5)_3\text{CO}\cdot\text{CH}_3$ , m.p.  $82^\circ$ . The ethers are very readily hydrolysed by acids. With sodium bisulphite, salts of triphenylmethyl sulphonic acid,  $(\text{C}_6\text{H}_5)_3\text{CSO}_3\text{Na}$ , are formed, and with aniline, triphenylmethyl-aniline is formed. It reacts with aniline hydrochloride forming *p*-aminotetraphenyl-methane (p. 551). With phenol and anisol tetraphenylmethane derivatives are formed in a similar way. The ease with which the carbinols are reduced to the hydrocarbons depends on the nature of the substituents in the benzene nucleus. Triphenylcarbinols containing a methoxy-group, particularly if in the *o*-position, are very readily converted into the corresponding triphenylmethane derivatives, even by formic acid (*Kauffmann*, Ber. 45, 768). The carbinols form coloured, unstable, acid sulphates with sulphuric acid. The stability of these compounds increases with the introduction of halogen or methoxyl into the benzene nucleus of the carbinol (*Baeyer*, Ber. 38, 1156). The well-defined crystalline perchlorates, which are highly coloured, are specially characteristic of the triphenylcarbinols. Triphenylcarbinol also forms salt-like compounds with pyridine and quinoline.

**Triphenyl-chloromethane**,  $(C_6H_5)_3CCl$ , m.p.  $111^\circ$ , is obtained from the carbinol by treatment with hydrochloric acid in glacial acetic acid, by the action of phosphorus pentachloride, or acetyl chloride (*Gomberg*, Ber. 36, 384, 3924), and by warming triphenylacetyl chloride with conc. sulphuric acid, when carbon monoxide is split off. It is obtained synthetically by the action of benzene on carbon tetrachloride in the presence of aluminium chloride (see *Norris*, Am. 26, 492). **Triphenyl-bromomethane**, m.p.  $152^\circ$ , is obtained by the action of bromine on a solution of triphenylmethane in carbon disulphide, in sunlight (*Allen*, Ann. 227, 110), or from the carbinol by the action of hydrobromic acid in glacial acetic acid (*Wieland*, Ber. 42, 3024). **Triphenyl-iodomethane**, m.p.  $132^\circ$ , is obtained by the action of a solution of iodine in carbon disulphide on a solution of triphenylmethyl (p. 575). When exposed to air, its solutions give triphenylmethylperoxide, with separation of iodine (see Vol. IV). **Triphenyl-fluoromethane**, m.p.  $102-104^\circ$ , is obtained by the action of acetyl fluoride on triphenylcarbinol (*Blicke*, Am. 46, 1515). The triphenyl-halogenomethanes combine with excess of the halogens to give well-crystallised perhalides, e.g.,  $(C_6H_5)_3CBr \cdot Br_2$ ,  $(C_6H_5)_3CBr \cdot I_2$ ,  $(C_6H_5)_3CI \cdot I_2$ , etc. (*Gomberg*, Ber. 35, 1831).

In the triphenyl-halogeno-methanes, the halogen is very loosely bound, and they behave in many ways as salts. Thus, their solutions in sulphurous acid, pyridine, and acetone conduct electricity. By electrolysis of a solution of triphenyl-bromomethane in liquid sulphur dioxide, the substance is broken down into bromine and the triphenylmethyl radical,  $(C_6H_5)_3C\cdot$ , which partly dimerises to hexaphenylethane (p. 575) (*Schlenk*, Ann. 372, 11). This behaviour is, of course, exactly analogous to what takes place with a metallic salt. When boiled with water, the triphenyl-halogeno-methanes pass smoothly into the triphenylcarbinol. When treated with silver acetate, triphenylcarbinol acetate,  $(C_6H_5)_3COCOCH_3$ , m.p.  $88^\circ$ , is formed (*Gomberg*, Ber. 36, 3926). With potassium cyanide, triphenyl-acetonitrile is formed (p. 557). Triphenyl-chloromethane reacts with primary alcohols in the presence of pyridine to give ethers of triphenylcarbinol ("trityl"-ethers), which often crystallise well. These reactions can be used for the purification and characterisation of primary alcohols, and has recently been employed in the investigation of sugars in order to obtain the configuration of the hydroxyl groups about the carbon atoms. The trityl ethers are fairly easily hydrolysed by treatment with methyl alcoholic hydrochloric acid (*Helferich*, Ber. 56, 766).

The triphenyl-halogeno-methanes, like all compounds of triphenylcarbinol with acids, can exist in two forms, which differ in colour. A colourless and a coloured form exist. Thus triphenyl-chloromethane, which is colourless in the solid state, dissolves in sulphur dioxide giving a yellow solution. The explanation is as follows: According to *Hantzsch* (Ber. 54, 2569, 2617) the two forms differ in the way in which they are affected by an electric current. The colourless, non-conducting form is regarded as a true ester ("pseudo"-salt), and the coloured compounds are true salts ("carbonium salts"). The colour, according to this view, is regarded as due to the transformation of the homopolar linkage into the ionic linkage, which is produced by an intramolecular change. According to *Lifschütz* (Ber. 64, 161) the coloured salts differ from the colourless compounds in molecular complexity, the former being associated complexes with a merquinoid system. The ease with which one form is converted into the other depends on the nature of the solvent. *Dilthey* (Ber. 62, 1834) formulate the coloured compounds as true salts with a coordinated unsaturated carbon atom in the cation, the coordinated linkage giving rise to the colour ("carbonium salts").

Triphenyl-chloromethane forms highly coloured compounds with aluminium, zinc, and stannic chlorides, etc., which correspond with the above-mentioned sulphates and perchlorates, and are regarded as carbonium (or carbenium) salts, with a complex anion. It reacts with magnesium in ether solution forming the very reactive triphenylmethyl-magnesium chloride  $(C_6H_5)_3CMgCl$ . By the action of zinc, or colloidal silver or copper on a benzene solution of triphenyl-chloromethane, in the absence of air, triphenylmethyl or hexaphenylethane is formed (see free radicals, Vol. IV). When heated above  $280^\circ$ , triphenyl-chloromethane and triphenyl-bromomethane condense to diphenylene-phenylmethane,  $(C_6H_5)_2CHC_6H_5$ .

**Triphenylmethyl-amine**,  $(C_6H_5)_3C \cdot NH_2$ , m.p.  $103^\circ$ , is obtained by passing ammonia gas into a benzene solution of triphenyl-halogeno-methane (*Nauen*,

Ber. 17, 442; *Hemilian*, Ber. 17, 741; *Gomberg*, Ber. 35, 1827). Triphenyl-methyl-aniline,  $(C_6H_5)_3C \cdot NHC_6H_5$ , m.p.  $144^\circ$  is obtained by warming triphenyl-carbinol with aniline in glacial acetic acid (*Elbs*, Ber. 17, 703; *Hemilian*, Ber. 17, 746; *Baeyer*, Ber. 35, 3016). The so-called diphenylbenzyl-sultam,

$C_6H_5 \begin{matrix} \swarrow [1]C(C_6H_5) \\ \searrow [2]SO_2 \end{matrix} NH$ , m.p.  $210^\circ$ , may be regarded as a derivative of triphenylmethyl-amine, since it is obtained, together with phenylbenzal-sultim (p. 516) by the condensation of pseudo-saccharin chloride with benzene in the presence of aluminium chloride (*Fritsch*, Ber. 29, 2296).

Triphenylmethyl-hydrazine,  $(C_6H_5)_3C \cdot NHNH_2$ , hydrochloride, m.p.  $133^\circ$ , is obtained together with *sym*-di-triphenylmethyl-hydrazine (see below) by the action of hydrazine hydrate on triphenyl-chloromethane. With nitrous acid it gives triphenylmethyl-azide,  $(C_6H_5)_3CN_3$ , m.p.  $64^\circ$ , a remarkably stable ester of hydrazoic acid (*Wieland*, Ber. 42, 3024).

Triphenylmethyl-hydroxylamine,  $(C_6H_5)_3CNHOH$ , is obtained by the action of hydroxylamine on triphenyl-chloromethane. It melts at  $130^\circ$  (*Mothwurf*, Ber. 37, 3152). When treated with phosphorus pentachloride it is converted into benzophenone-anil  $(C_6H_5)_2C=NC_6H_5$  (*Stieglitz*, Ber. 46, 2147).

*sym*-Triphenylmethyl-phenylhydrazine,  $(C_6H_5)_3CNHNHC_6H_5$ , m.p.  $137^\circ$ , is obtained by the action of phenylhydrazine on triphenyl-chloro- or triphenyl-bromo-methane. When acted upon by nitrous acid it forms triphenylmethane-azobenzene,  $(C_6H_5)_3CN:NC_6H_5$ , m.p.  $114^\circ$ .

*sym*-Ditriphenylmethyl-hydrazine,  $(C_6H_5)_3C \cdot NHNH \cdot C(C_6H_5)_3$ , m.p.  $219-220^\circ$ , is obtained by the action of hydrazine hydrate on triphenyl-chloromethane. When oxidised with sodium hypo-bromite it breaks down into nitrogen and triphenylmethyl, with the intermediate formation of the very unstable azotriphenylmethane, which has not itself been isolated. When treated with bromine or iodine it is converted into triphenylbromo- or -iodo-methane, and their perhalides (*Wieland*, Ber. 42, 3020). When heated above its melting point it breaks down into nitrogen and triphenylmethane. In the presence of stannous chloride at  $250-300^\circ$  it forms triphenylmethane and triphenylmethyl-imide, which immediately transforms to benzophenone-anil (see above) (*Stieglitz*, Am. 44, 1270).

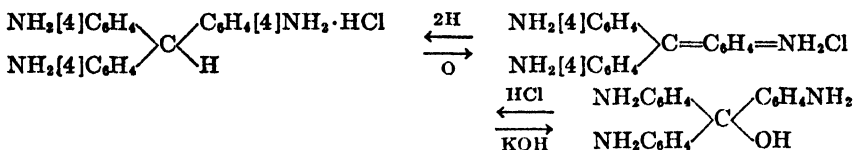
*m*- and *p*-Bromotriphenyl-carbinol, m.p.  $67^\circ$  and  $114^\circ$ , are obtained by the action of phenyl magnesium bromide on ethyl *m*- or *p*-bromobenzoate. *p,p',p'*-Trichlorotriphenyl-carbinol, m.p.  $99^\circ$ , is obtained from *p*-chloro-iodobenzene, ethyl *p*-chloro-benzoate, and magnesium. *p,p',p'*-Triiodotriphenyl-carbinol, m.p.  $163^\circ$ , is obtained by the action of iodine and potassium iodide on the tri-diazonium sulphate of pararosanine (*Baeyer*, Ber. 38, 585).

*m*- and *p*-Nitrotriphenyl-carbinol,  $(C_6H_5)_2C(OH)C_6H_4NO_2$ , m.p.  $75^\circ$  and  $98^\circ$ , respectively. The *p*-compound has been obtained in the pure state from its chloride, which is the condensation product of *p*-nitrobenzophenone chloride and benzene in the presence of aluminium chloride (*Tschacher*, Ber. 21, 190; *Baeyer*, Ber. 37, 604).

*p,p',p'*-Trinitrotriphenyl-carbinol,  $(NO_2[4]C_6H_4)_3C \cdot OH$ , m.p.  $171^\circ$ , is obtained by oxidising *p,p',p'*-trinitrotriphenylmethane with chromic acid in glacial acetic acid. When reduced it gives pararos-aniline.

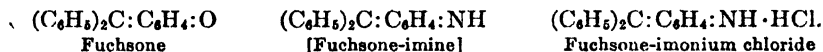
**AMINO-TRIPHENYL-CARBINOLS.** Of the compounds belonging to this class, *p,p'*-diaminotriphenyl-carbinol, and *p,p',p'*-triaminotriphenyl-carbinol, deserve special mention. *p,p'*-Tetramethyldiamino-triphenyl-carbinol is the base of malachite green, and *p,p',p'*-triaminotriphenyl-carbinol that of pararosanine. The free amino-carbinols are colourless. When they are warmed with acids colour-salts are formed with the elimination of water. These are also formed directly by the oxidation of the salts of the leuco-compounds, and are reconverted into the latter by reduction. Thus, when *p*-leuco-rosanine hydrochloride is oxidised it gives pararosanine

chloride, from which bases will separate the colourless *p,p',p''*-tri-amino-triphenyl-carbinol. With hydrochloric acid this again gives pararosaniline chloride:



Only those mono-, di-, and tri-aminotriphenyl-carbinols which contain at least one amino-group in the *p*-position can give rise to coloured salts with elimination of water. Dyes are only formed when there are *two* amino-groups in the *p*-position.

By careful decomposition of the dye-salt with caustic soda, the more or less unstable *methylene-quinone-imine* bases, of the type  $\text{Ar}_2\text{C}:\text{C}_6\text{H}_4:\text{NR}$ , or  $\text{Ar}_2\text{C}:\text{C}_6\text{H}_4:\text{NR}_2\text{OH}$  (*cf.* *methylene-quinones*, pp. 242, 340) are first formed. These pass into the amino-carbinols by addition of water, or transformation. If ammonia is used for the separation of the colour base an amine derived from triphenyl-methylamine is formed instead of the carbinol. These "amine-bases" are very similar to the carbinols. They are colourless, crystalline compounds, stable towards alkalis, and giving the dye when acted upon by acids, ammonia being removed (*Villiger*, *Ber.* 45, 2910). The dyes are reduced to the leuco-compounds by sodium hydrosulphite. In this reaction the leuco-sulphinic acids are first formed,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4)_3\text{C} \cdot \text{SO}_2\text{H}$ , which may also be formulated as sulphonylic acids. When heated, these intermediate products break down into the leuco-compounds and sulphite (*Wieland*, *Ber.* 52, 880; *Scheuing*, *Ber.* 56, 1583). These reactions are also given by the *p*-hydroxytriphenyl-carbinols (*cf.* pp. 539, 545). *Diphenylquino-methane* (p. 539) may be regarded as the parent substance of the triphenylmethane dyes. It is called fuchsone, after the most important dye of the series (*Baeyer*, *Ber.* 37, 2848):



This extended view of the triphenylmethane dyes as **imonium salts** with a meriquinoid system, is contrary to their formulation as carbonium salts. According to this latter view, the colour is due to the presence of a coordinated unsaturated C atom. The entry of a coordinate linkage into an ion deepens the colour (*Dilthey*, *Wizinger*, p. 529). According to this method, "fuchsone-imonium chloride" derived from fuchsone, would be formulated as a carbonium salt  $[(\text{C}_6\text{H}_5)_2\text{C}^*(\text{C}_6\text{H}_4 \cdot \text{NH}_2)]\text{Cl}$  (*Weygand*, *Ber.* 60, 2429; *Dilthey*, *Ber.* 62, 1834, 2078, 2738). It is not possible to bring forward evidence which would decide in favour of one or the other formulation. It is also possible that in the colour salts of the triphenylmethane dyes the charge of the cation may be carried by either the nitrogen or the carbon. In what follows, the more usual method quinoid-imonium formulation will be used. The coordination theory of these dyes has been dealt with by *Wizinger* in his book "Organische Farbstoffe" (Berlin and Bonn, 1933).

*p*-Amino-triphenyl-carbinol,  $\text{HO} \cdot \text{C}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{NH}_2$ , is obtained from its acetyl derivative, which is itself prepared by the oxidation of acetamino-triphenylmethane (p. 526) with lead dioxide; with hydrochloric acid it first forms the salts  $\text{HO} \cdot \text{C}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{NH}_2 \cdot \text{HCl}$  and  $\text{ClC}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{NH}_2 \cdot \text{HCl}$ , the former of which is faintly coloured, and the latter colourless. On heating, these lose water and hydrochloric acid, respectively, and become the salts of the oxygen-free base,

which are highly coloured. This compound, anhydro-*p*-aminotriphenyl-carbinol (fuchson-imine) is dimolecular in the free state, with the formula  $[(C_6H_5)_2C:C_6H_4:NH]_2$ , and is colourless. Its salts can be obtained as the condensation products of *p*-aminobenzophenone and phenyl magnesium bromide (*Baeyer*, Ber. 37, 597).

*p*-Anilino-triphenyl-carbinol, a colourless substance, is obtained by the addition of water to the anhydro-base, diphenyl-methylene-quinone-phenyl-imine,  $(C_6H_5)_2C:C_6H_4:NC_6H_5$ , also known as fuchson-anil. It forms red prisms, m.p. 133–138°. The latter is prepared by heating diphenyl-*p*-anisyl-methyl-anilide,  $(C_6H_5)_2C(NHC_6H_5)C_6H_4OCH_3$ , with organic acids (*e.g.*, benzoic acid) (*Baeyer*, Ber. 37, 608).

*p*-Dimethylamino-triphenyl-carbinol,  $(CH_3)_2N \cdot C_6H_4C(OH)(C_6H_5)_2$ , m.p. 93°, is obtained by the action of benzophenone on *p*-dimethylamino-phenyl magnesium bromide, or from benzophenone chloride, dimethylaniline, and zinc chloride (*Ehrlich*, Ber. 36, 4296; *Baeyer*, Ber. 37, 2857).

*o*-Amino-triphenyl-carbinol, m.p. 121°, is obtained from ethyl anthranilate and phenyl magnesium bromide. When heated for a long time it loses water and forms phenyl-acridine. When the hydrochloride of *o*-aminotriphenyl-chloromethane is treated with pyridine, the anhydro-compound analogous to the *p*-aminotriphenyl-carbinol,  $(C_{13}H_{15}N)_2$ , is formed. It melts at 250° with decomposition (*Baeyer*, Ber. 37, 3191).

*m*-Amino-triphenyl-carbinol, m.p. 155°, see *Tschacher*, Ber. 21, 190.

*p,p'*-Diamino-triphenyl-carbinol,  $(NH_2C_6H_4)_2C(OH)C_6H_5$ , colourless crystals, is best obtained by oxidising diaceto-diamino-triphenylmethane (p. 527) with manganese dioxide, hydrolysing, and purifying through the methyl ether, m.p. 161–163°. When heated water is eliminated and it passes into the unstable methylene-quinone-imine base (amino-fuchson-imine). The salts of this compound are violet-red in colour, and resemble fuchsine (*Baeyer*, Ber. 37, 2859).

*p,p'*-Dimethyl-diamino-triphenyl-carbinol,  $(CH_3NH \cdot C_6H_4)_2C(OH)C_6H_5$ , m.p. 95°, is obtained by hydrolysis of the cyanogen-substituted carbinol,  $[CH_2N(CN) \cdot C_6H_4]_2C(OH)C_6H_5$ . This compound itself is obtained from the corresponding triphenylmethane derivative (p. 527) by oxidation with permanganate in acetone solution (*von Braun*, Ber. 37, 641).

*p,p'*-Tetramethyl-diamino-triphenyl-carbinol,  $C_6H_5 \cdot C(OH)(C_6H_5 \cdot [4]N(CH_3)_2)_2$ , m.p. 132°, crystallises from benzene in colourless crystals. It is obtained from the salts of the corresponding quinoid ammonium base, malachite green, by precipitation with alkali. It is also prepared by the oxidation of an alcoholic solution of *p,p'*-tetramethyl-diamino-triphenylmethane with chloranil (*Fischer*, Ann. 206, 130) and by the action of ethyl benzoate on *p*-dimethylamino-phenyl magnesium bromide (*Ehrlich*, Ber. 36, 4296).

Methyl ether,  $C_6H_5C(OCH_3)[C_6H_4N(CH_3)_2]_2$ , m.p. 151° (*Fischer*, Ber. 33, 3356; *Baeyer*, Ber. 37, 2867). Iodomethylate,  $C_6H_5C(OCH_3)[C_6H_4N(CH_3)_2]_2 + 2H_2O$ , is obtained by heating *p,p'*-diamino-triphenyl-carbinol and *p,p'*-tetramethyl-diamino-triphenyl-carbinol with methyl iodide and methyl alcohol.

If *p,p'*-tetramethyl-diamino-triphenyl-carbinol is decomposed by acids, it dissolves in the cold to give an almost colourless solution. On long standing, or more rapidly on warming, it changes to a green colour, with formation of green salts of the quinoid ammonium base, malachite green (*Fischer*, Ber. 12, 2348; *Hantzsch*, Ber. 33, 298).

Malachite green,  $C_6H_5C \begin{array}{l} \nearrow C_6H_4N(CH_3)_2 \\ \searrow C_6H_4=N(CH_3)_2Cl \end{array}$ , is obtained by the action of zinc chloride on a mixture of benzotrichloride and dimethylaniline, or on a mixture of benzoyl chloride and dimethylaniline (*Fischer*, Ann. 206, 137).

In commerce, leuco-malachite green is first formed, and its hydrochloride is oxidised by lead dioxide. While benzoic acid itself will not condense with dimethylaniline, the ortho-methylated benzoic acids condense smoothly with tertiary anilines to form green dyes corresponding to malachite green (Ger. Pat. 101,426).

In trade, malachite green comes on the market chiefly as its double salt with zinc chloride,  $(C_{23}H_{23}N_2Cl)_2 \cdot 2ZnCl_2 + 2H_2O$ , or as the oxalate,  $(C_{23}H_{23}N_2)_2 \cdot 3H_2C_2O_4$ .

**History.**—Malachite green was obtained by O. Fischer in 1877 by the oxidation of *p,p'*-tetramethyl-diamino-triphenyl-methane. He had obtained this compound by the condensation of benzaldehyde with dimethylaniline. In 1878 Doebner discovered the preparation of malachite green from benzotrichloride and dimethylaniline.

**Brilliant green, solid green, or new Victoria green**, is prepared from diethylaniline and benzaldehyde. It is the *tetra-ethyl* derivative corresponding to malachite green (Fischer, Ber. 14, 2521). The colour is rather more yellowish than malachite green.

**Acid green** is obtained from benzaldehyde and benzyl-ethyl aniline by condensation, oxidation, and sulphonation. The sulphonic acid group is in the benzyl radical (Friedländer, Ber. 22, 588).

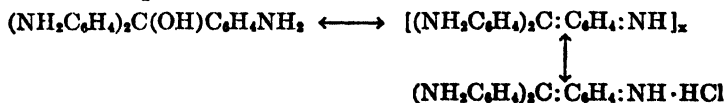
**Nitro-malachite green** is obtained from *o*-, *m*-, and *p*-nitrobenzaldehyde and dimethylaniline (Fischer, Ber. 15, 682). *o*-Amino-malachite green has a blue colour. The colour base is obtained by oxidation and hydrolysis of the *urethane* of 2-amino-leuco-malachite green,  $C_7H_5O_2C \cdot NH[2]C_6H_4CH[C_6H_4 \cdot N(CH_3)_2]_2$  (Baeyer, Ber. 36, 2776). Alkoxy-malachite greens and their derivatives have been obtained from substituted aryl-magnesium halides and Michler's ketone (p. 519), or by the action of dimethylaniline magnesium bromide and methyl anisate (Votocek, Ber. 46, 1755, 1760). For other substituted malachite greens, see Noelting, Ber. 39, 2041.

*o,p'*-, *m,p'*-, *o,m'*-, and *m,m'*-Tetramethyl-diamino-triphenyl-carbinol, m.p. 170°, 140°, 184°, and 129°, are obtained from the corresponding amino-benzophenones by reaction with phenyl magnesium bromide, or dimethylaniline magnesium iodide (Baeyer, Ann. 354, 195).

Various patent blues have been prepared, which are sulphonated malachite greens. They show greater fastness to alkalis than does malachite green itself.

### *Triamino-triphenyl-carbinols*

*p,p',p''*-Triamino-triphenyl-carbinol, *p,p',p''*-triamino-diphenyl-*m*-tolyl-carbinol, and their methylated, ethylated, benzylated, and phenylated derivatives are of outstanding importance in the coal-tar dye industry. Their salts with one equivalent of an acid—hydrochloric or acetic—form the group of rosaniline dyes, in the narrower sense. Like malachite green, the rosaniline dyes contain no carbinol oxygen, since salt formation is accompanied by an intramolecular anhydride or methylene-quinone-imine formation (see p. 531). The free carbinols liberated from the salts by alkalis are colourless, but turn red in air. By careful treatment of pararosaniline with caustic soda a polymer of the oxygen-free methylene-quinone-imine base (*p,p'*-diamino-fuchson-imine) is formed first, in slightly coloured needles. On the other hand, if *p,p',p''*-triamino-triphenyl-carbinol is heated in a current of hydrogen to 200°, an oxygen-free base is obtained as a red amorphous mass. This substance quantitatively regenerates pararosaniline with acids (Baeyer, Ber. 37, 1183, 2867). The following scheme shows these relationships:



**Fuchsine** (Z. angew. Chem. 1899, 1034) is the dye obtained by the oxidation of a mixture of aniline, *o*-toluidine, and *p*-toluidine, known as red oil. The chief constituent of fuchsine is **rosaniline**, the hydrochloride or acetate of anhydro-*p,p',p''*-triamino-diphenyl-*m*-tolylcarbinol,  $C_{20}H_{19}N_3 \cdot HCl + 4H_2O$  or  $C_{20}H_{19}N_3 \cdot C_2H_4O_2$ . The salts with one equivalent of acid combine with two further equivalents of acid to give black salts, which are decomposed in water to give the intensely coloured monobasic salts. The latter, the dyes, are usually readily soluble in water and alcohol, and crystallise in coppery-green crystals with a metallic lustre. Their solutions are carmine in colour, and dye wool and silk immediately a violet red colour. Vegetable fibres such as cotton can be dyed after treatment with a mordant, such as tannin.

The mono- and tri-basic salts of rosaniline will take up 4HCl,  $NH_3$ , or  $H_2O$  forming colourless compounds, which readily pass into the original substance, the addendum being split off. The colour is also restored by converting the amino groups into quaternary ammonium bases (Brand, J. pr. [2], 118, 97).

Fuchsine combines with sulphurous acid to give a colourless, readily soluble compound, fuchsine sulphurous acid (for constitution, see Hantzsch, Ber. 33, 289; Wieland, Ber. 54, 2527). The colourless solution is turned red by addition of aldehydes, and is used as a reagent for their detection.

In the oxidation of "red oil," stannic chloride (Verquin, 1859), mercurous or mercuric nitrates, or arsenic acid at 180–200° (Medloc; Nicholson; Girard, de Laire, 1860) may be used. Nitrobenzene with a little ferric chloride, or ammonium vanadate at 180–190°, may also be employed, when half the "red oil" is available as hydrochloride (Coupier, 1869, cf. Bruning, Ber. 6, 25, 1072; Coupier, Ber. 6, 423).

In the arsenic acid process the fuchsine is obtained in the form of its arsenate, which is converted into the hydrochloride or acetate, and freed from arsenic acid by recrystallization.

The nitrobenzene process has the advantage of producing a non-poisonous fuchsine directly. Nitrobenzene acts merely as an oxidising agent, and does not take part in the formation of the fuchsine.

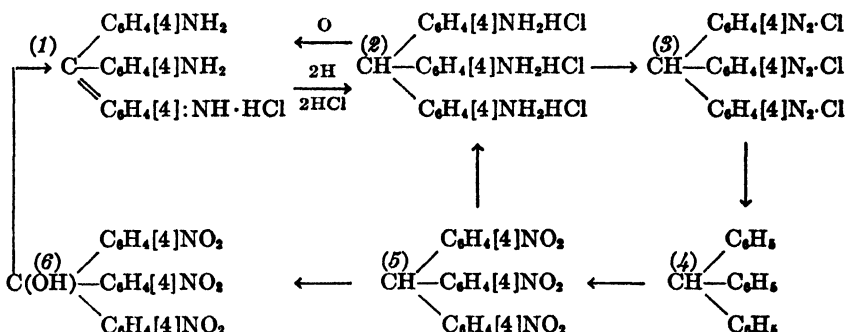
Fuchsine is not formed from aniline, *p*-toluidine, or *o*-toluidine alone, and a mixture of aniline and *o*-toluidine gives no fuchsine on oxidation. On the other hand, not only does a mixture of the three amines give fuchsine, but a mixture of aniline with *p*-toluidine gives, on oxidation, a dye which has the properties of fuchsine, and is called pararosaniline. The latter is also present in small proportion when the mixture of the three amines is oxidised. The chief constituent of fuchsine is the next higher homologue of pararosaniline, rosaniline (Fischer, Ber. 13, 2204).

*By-products in the manufacture of fuchsine.*—In the fuchsine melt there are, in addition to about 34% fuchsine, some brown and violet dyes; mauvaniline, violaniline, substances possibly belonging to the indulins, and other substances not yet thoroughly investigated. There is also present a small quantity of a yellow acridine dye, phosphine, or chrysaniline.

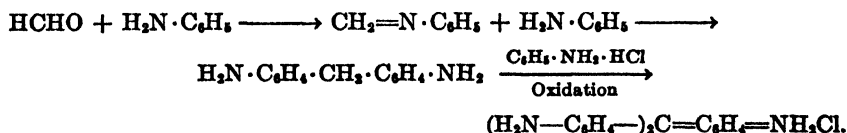
*History of the knowledge of the constitution of rosaniline and pararosaniline.*—The first to concern himself with the scientific investigation of fuchsine was A. W. Hofmann. His work, carried out in the early 1860's, led him to propose a formula for fuchsine and its colour base. He discovered numerous derivatives of fuchsine, particularly the methylated and ethylated violet fuchsines. Hofmann supposed that the nitrogen atoms held the radicals in the fuchsine molecule together. In 1867, however, Kekulé put forward the possibility that the methyl group of the toluidine molecule which was necessary for the production of fuchsine, held the molecule together. Z. Kulowsky (1869) assumed that there were three amino-groups in fuchsine, and regarded it as a derivative of the hydrocarbon  $C_{18}H_{14}$ . It was gradually recognised that fuchsine was a derivative of a higher hydrocarbon. This view originated with the experiments of Wanklyn, Caro, Graebe, Dale, Schorlemmer, and others, which were particularly concerned

with the relationship between fuchsine and rosolic acid. The "keystone to that extended series of experimental and speculative investigations" was the conversion of pararosaniline, prepared from a mixture of aniline and *p*-toluidine by oxidation, into triphenylmethane by *O.* and *E. Fischer* (1878). The hydrocarbon they prepared from rosaniline the chief constituent of fuchsine, turned out to be diphenyl-*m*-tolylmethane.

Triphenylmethane (4) is obtained by the decomposition of the tridiazonium sulphate of *p*-leucoaniline with alcohol. In the diagram below, the formula of the tridiazonium chloride (3) of *p*-leucoaniline (2) is used for the sake of simplicity. Concentrated nitric acid converts triphenylmethane into *p,p',p''*-trinitro-triphenylmethane (5), which, on reduction, gives *p,p',p''*-triamino-triphenylmethane or *p*-leucoaniline (2), and on oxidation *p,p',p''*-trinitro-triphenylcarbinol (6). When *p*-leucoaniline is oxidised with arsenic acid, or when *p,p',p''*-trinitrotriphenylcarbinol is reduced with acetic acid and zinc dust, pararosaniline (1) is formed. The following diagram illustrates this series of reactions, which were carried out starting with rosaniline itself (*Fischer*, *Ann.* 194, 242).



**Pararosaniline** is produced by oxidising a mixture of aniline and *p*-toluidine by arsenic acid, or nitrobenzene (p. 533). The reaction may be supposed to take place by the primary oxidation of a molecule of *p*-toluidine to methylene-quinone imine, or *p*-aminobenzaldehyde. This then condenses with 2 molecules of aniline to *p*-leucoaniline or *p,p',p''*-triamino-triphenylmethane (p. 527), from which, finally, rosaniline is formed by oxidation. In the "new fuchsine process" (*Homolka*) the preparation of pararosaniline starts from aniline and formaldehyde. The Schiff's base first formed is converted by heating with aniline and aniline hydrochloride into *p,p'*-diamino-diphenylmethane, which, on treatment with aniline in the presence of an oxidising agent, is converted into parafuchsine:



On the small scale, the most convenient way of oxidising aniline and *p*-toluidine to pararosaniline is to use mercuric chloride (*Goldberg*, *Ber.* 24, 3552). An interesting method of making pararosaniline is to heat aniline with carbon tetrachloride to 230°, when the latter furnishes the linking carbon atom. If iodoform is used, the hydriodide of pararosaniline is formed.

Pararosaniline is also formed by the reduction of *p,p',p''*-trinitro-triphenylcarbinol (see above), by heating *p,p',p''*-nitro-diamino-triphenylmethane with ferrous chloride (*Fischer*, *Ber.* 15, 678). Triamino-triphenylcarbinol can also



be made by reduction of *p*-nitro-diamino-triphenylmethane with zinc dust. In this case the diamino-diphenyl-methane-phenylhydroxylamine,  $(C_6H_4NH_2)_2CH \cdot C_6H_4 \cdot NHOH$ , rearranges as soon as it is formed (*Prudhomme*, C.r. 121, 891); see also the action of sodium hydroxide on nitro-diamino-triphenylmethane (*Prudhomme*, Bull. soc. ch. [3], 17, 643). It can also be made from formaldehyde, aniline, and phenylhydroxylamine (Ger. Pat. 105,198), by heating *p*-diamino-diphenylmethane with an oxidising agent (*Gram*, Ber. 25, 302), by heating *p*-nitrobenzalchloride with aniline, and by heating aurine to 120° with ammonium hydroxide (*Dale*, Ber. 10, 1016, 1123).

Nitrous acid converts pararosaniline into aurine. If the diazonium chloride or pararosaniline is acted upon by copper powder, triphenyl-carbinol is formed. (*Fischer*, Ber. 26, 2225). Concentrated hydriodic acid at 180–200° converts it into aniline and *p*-toluidine. Evidence in favour of the para position of the two amino-groups is furnished by the conversion of pararosaniline into *p,p'*-diamino-benzophenone by boiling with hydrochloric acid. This compound is also obtained from *p*-diamino-triphenylmethane, the condensation product of benzaldehyde and aniline. Paraleucoaniline, the reduction product of pararosaniline, is formed by the reduction of *p,p',p'*-nitro-diamino-triphenylmethane. The para position of the three groups in this compound is proved by the fact that it can be obtained by the same condensation reaction between *p*-nitrobenzaldehyde and aniline.

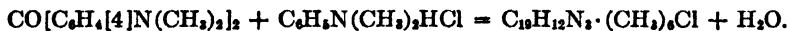
The salts of rosaniline give a deeper blue shade than those of pararosaniline.

**Rosaniline sulphonic acid**, *acid fuchsine*, or *fuchsine S*, is produced by the action of fuming sulphuric acid on rosaniline at 120°. For nuclear substituted fuchsines, see *Finger*, J. pr. [2], 79 492.

### Alkylated Pararosanilines

The introduction of methyl groups into the amino groups of pararosaniline results in the formation of violet dyes, such as *methyl violet*. The violet colour takes on a more bluish tinge as the number of methyl groups is increased. These dyes can also be obtained by oxidation of dimethylaniline. The methyl violets are reduced to leuco-compounds by sodium hydrosulphite, or by heating with ammonium sulphide to 120° (*Fischer*, J. pr. 79, 562). Boiling hydrochloric acid resolves then into dimethylaniline and methylated *p*-diamino-benzophenones (*Wickelhaus*, Ber. 19, 108). In addition to their use for dyeing silk, wool, and mordanted cotton, they are used in the manufacture of ink, and in medicine as disinfectants.

**Hexamethyl-pararosaniline**, *crystal violet*,  $[(CH_3)_2N \cdot C_6H_4]_2C : C_6H_4 : N(CH_3)_2Cl$ , differs from the lower homologues by the great ease with which it crystallises. It is one of the chief constituents of methyl violet. It is obtained (1) by the condensation of *p,p'*-tetramethyl-diamino-benzophenone and dimethylaniline hydrochloride in the presence of dehydrating agents:



(2) By heating dimethylaniline with carbonyl chloride, and aluminium or zinc chlorides (Ger. Pat. 29,943). Formic acid, ethyl formate, ethyl chlorocarbonate, perchloromethyl mercaptan, etc., will act in the same way as the carbonyl chloride in this reaction (*Wickelhaus*, Ber. 19, 109). (3) By oxidation of *p,p'*-tetramethyl-diaminodiphenylmethane with dimethylaniline. (4) By heating its chloro- or iodo-methylate to 110–120°. (5) By oxidation of its leuco-base.

*p,p',p'*-Hexamethyl-triamino-triphenylmethane, leuco-crystal violet,  $CH-[C_6H_4[4]N(CH_3)_2]_3$ , m.p. 173° is obtained by the reduction of crystal violet, by the condensation of ethyl orthoformate and dimethylaniline with zinc chloride, by condensation of *p,p'*-tetramethyl-diamino-diphenyl carbinol with dimethylaniline, and by the condensation of formamide chloride with dimethylaniline

when tetramethyl-diamino-benzhydrylamine (see p. 513) may be formed as an intermediate product (Ger. Pat. 105,198).

*p,p',p''*-Hexamethyl-triamino-triphenyl-carbinol, crystal violet leuco-hydrate,  $C(OH)[C_6H_4[4]N(CH_3)_2]_3$ , m.p. 195°, is obtained by the condensation of *p*-dimethyl-amino-phenyl magnesium bromide with *p,p'*-tetramethyl-diamino-benzophenone (Ehrlich, Ber. 36, 4297). For the perbromide, see Rosenheim, Ber. 36, 753.

Like the introduction of methyl groups into the amino groups of pararosaniline, substitution of nuclear hydrogen by methyl deepens the colour. For homologues of crystal violet, and their characteristics as dyes, see Kassow, J. pr. [2], 85, 497.

**Methyl violet** is a mixture of hexamethyl-pararosanine with lower methylated pararosanilines (Wickelhaus, Ber. 19, 107). It is produced by the oxidation of dimethylaniline either alone, or mixed with monomethylaniline, by iodine, chloranil, or copper sulphate or chloride. If copper chloride is used it is advisable to add acetic acid or phenol.

**Pentamethyl-violet**,  $C_{19}H_{12}N_3(CH_3)_5HCl$ , is obtained by oxidation of *p,p',p''*-pentamethyl-triamino-triphenylmethane  $[(CH_3)_2NC_6H_4]_2CH \cdot C_6H_4[4]NH \cdot CH_3$ , m.p. 116°, which can be obtained by reduction of commercial methyl violet, a mixture of penta- and hexamethyl violet, through the acetyl derivative. This gives, on oxidation, a green dye (Fischer, Ber. 16, 2906).

**Tetramethyl violet** is obtained by the oxidation of *p,p',p''*-amino-tetramethyl-diamino-triphenylmethane,  $NH_2[4]C_6H_4CH[C_6H_4[4]N(CH_3)_2]_2$ , m.p. 152°, which has been obtained by the reduction of *p*-nitromalachite green (p. 533), and whose acetyl derivative, like that of pentamethyl-paraleucoaniline (see above) gives a green dye on oxidation.

**Methyl green**,  $Cl(CH_3)_2N[4]C_6H_4C \begin{matrix} \swarrow C_6H_4[4]N(CH_3)_2 \\ \searrow C_6H_4[4]N(CH_3)_2 \end{matrix}$ , is produced by the action of methyl chloride on an alcoholic solution of methyl violet warmed to 40°, with gradual addition of caustic soda.

### Alkylated Rosanilines

If rosaniline is heated with methyl iodide, methyl chloride, ethyl iodide, or ethyl chloride, and methyl or ethyl alcohol, three hydrogen atoms of the amino-groups are replaced by methyl or ethyl radicals. The methyl base yields reddish-violet salts, whilst the ethyl base gives pure violet salts, known as Hofmann's violet and as dahlia. These are difficultly soluble in water, but dissolve readily in alcohol.

The violet dyes, by taking up further methyl or ethyl groups, give tetra-alkylated rosaniline iodides which will still add on a molecule of methyl or ethyl iodide forming **iodine green**, the iodomethylate of tetramethyl-roosaniline iodide,  $C_{20}H_{16}(CH_3)_3N \cdot CH_2I + H_2O$  (Miller, Ber. 28, 1008). Both iodine green and methyl green have been largely replaced in industry. Both types of dye possess, however, a certain theoretical interest. They contain an amino-group which is fully alkylated, and therefore coordinated. This amino-group can no longer act as an auxochrome. In consequence, the violet colour of methyl violet is displaced to the green of malachite green.

Another green rosaniline dye, **aldehyde green** (Usebe, J. pr. 92, 337), is obtained by heating rosaniline with aldehyde and sulphuric acid, and by further action of sodium hyposulphite. For its constitution, see Miller, Ber. 24, 1700; Ber. 29, 60).

*Phenylated Pararosanilines*

When diphenylamine is heated with carbon chloride,  $C_2Cl_6$ , or oxalic acid to  $120^\circ$ , **diphenylamine blue** is obtained. This substance has also been obtained by fusing pararosaniline with aniline in the presence of benzoic acid at  $180^\circ$  (*Hansdörfer*, Ber. 23, 1964). By heating trianisyl carbinol (p. 542) with aniline and benzoic acid, the benzoate of the pure colour base is formed. The latter, called **dianilino-fuchso-anil**,  $(C_6H_5NH \cdot C_6H_4)_2C : C_6H_4 : NC_6H_5$ , is a black powder, m.p.  $238^\circ$ , which gives the colourless *p,p',p''*-trianilino-triphenyl-carbinol by taking up water, and trianilino-triphenylmethane on reduction (*Baeyer*, Ber. 37, 2870). At present, only the sodium salts of the mono- and di-sulphonic acids of diphenylamine blue are used in industry under the names of alkali blue and water blue (cotton blue), respectively.

When diphenylmethylaniline,  $(C_6H_5)_2N \cdot CH_3$ , is acted upon by ethyl perchloro-carbonate,  $Cl \cdot CO_2 \cdot Cl$ , **trimethyl-triphenyl-pararosaniline**,  $C(OH)[C_6H_4N(CH_3)C_6H_5]_3$ , is formed (Ger. Pat. 34,607). Similarly, when triphenylamine is treated with carbonyl chloride, the hydrochloride of **hexaphenyl-pararosaniline**,  $C(OH)[C_6H_4 \cdot N(C_6H_5)_2]_3$ , is formed (*Heydrich*, Ber. 19, R 758). When carbazole or diphenylene-imide is heated with oxalic acid, **tricarbazol-carbinol**,  $C(OH)(C_{12}H_7NH)_3$ , is formed (*Bamberger*, Ber. 20, 1904).

*Phenylated Rosanilines*

These are obtained by heating rosaniline hydrochloride with aniline or the toluidines, or the free base with aniline and some benzoic acid. The hydrochloride of **triphenyl-roosaniline**,  $C_{20}H_{16}(C_6H_5)_3N_3 \cdot HCl$ , appeared in commerce as aniline blue (spirit blue). It is a bluish-brown powder with a coppery lustre, soluble in alcohol, but not in water. To make it soluble in water, sulphonic salts are made, various shades of blue being produced according to the extent of sulphonation. These dyes are known as *soluble blue*. At present they have been replaced by other dyes. When triphenyl-roosaniline is dry distilled, diphenylamine is formed.

By converting rosaniline, through the tri-diazonium compound, into the **tri-hydrazine derivative**, *roshydrazine*,  $(C_6H_4NH \cdot NH_2)_2C(OH)C_6H_5(CH_3)NHNH_2$ , is formed, from which red and blue dyes have been obtained by condensation with aldehydes and ketones.

Further hexamethyl-triamino-triphenyl carbinols have been prepared by the reaction of ethyl dimethyl-aminobenzoate with *p*-dimethyl-aminophenyl magnesium iodide,  $(CH_3)_2NC_6H_4MgI$  (*Baeyer*, Ann. 354, 200).

## (d) Phenol Derivatives of the Triphenylmethanes

The phenol derivatives of the triphenylmethanes are produced (1) from the corresponding amino compounds, through the diazonium salts; (2) by condensations similar to those entered into by the amino-compounds, if phenols are substituted for anilines; (3) by reduction of phenol-carbinols, into which they are converted on oxidation.

**MONOHYDROXY-TRIPHENYLMETHANES.** *o*-Hydroxy-triphenylmethane,  $(C_6H_5)_2CH \cdot C_6H_4[2]OH$ , m.p.  $124^\circ$ , is obtained from *o*-aminotriphenylmethane (*Fischer*, Ann. 241, 367) or by reduction of the carbinol. *m*-Hydroxy-triphenylmethane, m.p.  $106^\circ$  (*Baeyer*, Ann. 354, 171). *p*-Hydroxy-triphenylmethane, m.p.  $110^\circ$ , is obtained by the action of diphenyl-chloromethane on phenol, and transposition of the *O*-ether first produced with the aid of zinc chloride or hydrochloric acid (*van Alphen*, Rec. 46, 799). It dissolves readily in 50% acetic acid giving a yellow solution, which is perhaps due to the presence of a quinoid system (*Anderson*, Am. 50, 203).

*o*-Cresyl-diphenylmethane,  $(C_6H_5)_2CHC_6H_3[3]CH_3[4]OH$ , m.p.  $100^\circ$ , is obtained from diphenyl carbinol, *o*-cresol, and stannic chloride (*Bistrzycki*, Ber. 35, 3137; 36, 3561). By condensation of salicylaldehyde and anisaldehyde with

aniline sulphate, or dimethylaniline and zinc chloride, **hydroxy-diamino-triphenylmethane** is obtained (*Fischer*, Ber. 14, 2522; *Renouf*, Ber. 16, 3107).

The di- and tri-hydroxy-triphenylmethanes give di- and tri-phenol carbinols on oxidation. These are usually dyes. Carbinols in which two benzene nuclei are hydroxylated, and which correspond to the malachite green compounds, are called *benzeins* (p. 540); the corresponding dihydroxy-triphenylmethanes are leucobenzeins. Those carbinols hydroxylated in three benzene nuclei are called *aurines* or *rosolic acids*, and the corresponding trihydroxy-triphenylmethanes leucaurines or leucorosolic acids.

***p,p'*-Dihydroxy-triphenylmethane**, leucobenzein, or leucobenzaurine,  $C_6H_5CH(C_6H_4[4]OH)_2$ , m.p. 161°, is obtained (1) from *p,p'*-diamino-triphenylmethane (p. 526) (*Fischer*, Ann. 206, 153); (2) by condensation of benzaldehyde and phenol with sulphuric acid (*Russanow*, Ber. 22, 1944); (3) by reduction of benzaurine (*Doehner*, Ann. 217, 230). **Dihydroxy-dimethyl-triphenylmethane**,  $C_6H_5CH[C_6H_4(OH)CH_3]_2$ , m.p. 170° (*Schroeter*, Ann. 257, 70). **Phenyl-dithymol-methane**, m.p. 166°.

For the condensation of *m*-nitrobenzaldehyde with phenols, see *Bertini*, Gazz. 21, 167).

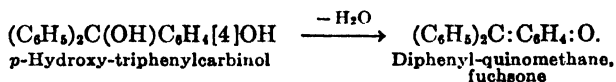
***p,p',p''*-Trihydroxy-triphenylmethane**, leucaurine,  $CH(C_6H_5[4]OH)_3$ , is obtained by the reduction of aurine, its carbinol-anhydride, with zinc dust and caustic soda or acetic acid. Colourless prisms, which turn red in air (*Dale*, Ann. 166, 286; *Zulkowsky*, Ann. 194, 136; 202, 198). Triacetate, m.p. 138° (*Caro*, Ber. 11, 1117). ***p,p',p''*-Trianisylmethane**,  $(CH_3O[4]C_6H_4)_3CH$ , m.p. 45–47°, is obtained from anisaldehyde and anisole with a mixture of acetic and sulphuric acids (*Baeyer*, Ber. 35, 1197).

**Leucorosolic acid**,  $(HO[4]C_6H_4)_2CH \cdot C_6H_5[4]OH[3]CH_3$ , is produced in the reduction of rosolic acid. Triacetate, m.p. 148° (*Graebe*, Ann. 179, 198).

### (e) Phenol Derivatives of Triphenyl-carbinol

These substances are produced by the oxidation of the hydroxy-triphenylmethanes or their ethers, and they can also be obtained by the direct, synthetic, general methods for the triaryl-carbinols (p. 528).

The *p*-hydroxylated triaryl-carbinols split off water more or less readily, and pass into methylene-quinones or diaryl-quinomethanes (see fuchson, p. 531). By heating *p*-hydroxytriphenyl-carbinol, diphenyl-quinomethane is formed. This substance may be regarded as the parent substance of the triphenylmethane series of dyes:



### A. Triphenyl-carbinols Hydroxylated in One Benzene Nucleus

***o*-Hydroxy-triphenyl-carbinol**, m.p. 140°, is obtained from ethyl salicylate and phenyl magnesium bromide. When distilled *in vacuo* it gives phenyl-xanthone. ***m*-Hydroxy-triphenyl-carbinol**, m.p. 148° (*Baeyer*, Ann. 354, 167). ***p*-Hydroxy-triphenyl-carbinol**, two forms, m.p. 139° and 165°, are obtained from *p*-hydroxy-triphenylacetic acid by splitting off carbon monoxide by means of sulphuric acid. The compound can also be obtained from the methyl ether, *p*-anisyl-diphenyl-carbinol, m.p. 84°, which is itself the condensation product of ethyl anisate and phenyl magnesium bromide. ***p*-Hydroxy-triphenyl-carbinol**, and ***p*-methoxy-triphenyl-chloromethane** on heating to 200°, split off water and methyl chloride, respectively, with formation of **diphenyl-quinomethane**, or fuchson, an orange

crystalline substance, m.p. 168°. This readily passes into the carbinol again by taking up water. In a similar way, diphenyl-dibromo-quinomethane is obtained from hydroxy-dibromo-triphenyl-carbinol, and diphenyl-methyl-quinomethane from diphenyl-*o*-cresol-carbinol. Diphenyl-quinomethane is also formed by the condensation of diphenyl-ketene with excess of a quinone, by removing carbon dioxide from the  $\beta$ -lactones first formed (p. 555). 2,5-Dihydroxy-triphenyl-carbinol, m.p. 136°, is obtained from ethyl gentisate and phenyl magnesium bromide. 3,4-Dihydroxy-triphenyl-carbinol, obtained by condensation of benzophenone chloride with catechol in the presence of sulphuric acid, gives 3-hydroxy-fuchsonone on heating, water being eliminated. The last-mentioned compound melts at 123° (Baeyer, Ann. 372, 82).

For the methyl ethers of hydroxy-triphenyl-carbinols, see Lund, Am. 49, 1346.

### B. Benzeins

These are produced by the condensation of benzotrichloride with mono- and polyhydric phenols in which the *p*-position to the hydroxyl is not substituted, e.g., *o*- and *m*-cresol, resorcinol, and catechol, but not *p*-cresol, hydroquinone, etc. (Doebner, Ann. 257, 56), which if they react at all, give only very slight yields (Kehrmann, Ann. 372, 342). Aromatic hydroxy-compounds will condense with benzyl alcohol in the presence of concentrated sulphuric acid at 140–150°, or of chloroform, carbon tetrachloride, iodoform, or zinc chloride, to give benzeins (Sen, Am. 47, 1079; J. Indian Chem. Soc. 1, 303). They are also formed by oxidation of their leuco-compounds, the corresponding hydroxy-triphenyl-methanes. See also p. 539.

The benzeins are usually red substances, with a metallic lustre, which dissolve when boiled with sodium sulphite solution, and are reprecipitated by the addition of acids. They dissolve in alkalis giving a red or violet colour with formation of quinoid salts, such as  $O:C_6H_4:C(C_6H_5)_2C_6H_4ONa$ . These are decomposed even by the carbon dioxide of the air, and with large quantities of alkalis lose their colour, giving the carbinols.

*p,p'*-Dihydroxy-triphenyl-carbinol, phenolbenzein, or benzaurine,  $C_6H_5C(OH)(C_6H_4OH)_2$ , is produced (1) by the oxidation of *p*-dihydroxy-triphenyl-methane, into which it is reconverted by reduction; (2) by condensation of benzotrichloride with phenol, analogous to the formation of malachite green (Doebner, Ann. 217, 223). It is a brick-red, crystalline powder. It decomposes on fusion with alkalis, giving first benzene and *p,p'*-dihydroxy-benzophenone, and then *p*-hydroxybenzoic acid and phenol. Diacetate, m.p. 119°; dimethyl ether, phenyl-*p,p'*-dianisyl-carbinol, m.p. 77°, is obtained from phenyl-dianisyl-methane, the condensation product of benzaldehyde and anisole. It gives benzaurine when boiled with dilute sulphuric acid (Baeyer, Ber. 36, 2791). Benzaurine may also be regarded as a molecular compound of *p*-hydroxyfuchsonone and water (Pfeiffer, Ber. 56, 98). It forms a crystalline, unstable compound with sodium bisulphite, and readily reacts with bromine forming tetrabromo-benzaurine (Meyer, Ber. 57, 591).

*p,p'*-Dihydroxy-*m,m'*-dimethyl-triphenyl-carbinol, *o*-cresol-benzein,  $C_6H_5C(OH)[C_6H_3(3)CH_3(4)OH]_2$ , m.p. 220–225° (Schroeter, Ann. 257, 69), can be regarded as a molecular compound of dimethyl-*p*-hydroxyfuchsonone with water (Meyer, Ber. 57, 1360; Orndorff, Am. 49, 992). Further dihydroxy-triphenyl-carbinols have been obtained from the corresponding dihydroxy-benzophenones by the action of phenyl magnesium bromide (Baeyer, Ann. 354, 177).

The *o,o'*-dihydroxy-triphenyl-carbinols are only known in the form of their

anhydrides, the phenyl-xanthidrols,  $C_6H_5 \cdot C(OH) \begin{matrix} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{matrix} O$ . Those com-

pounds which are substituted with OH or NH<sub>2</sub> in the *p*-position to the central carbon atom are of special interest, as they pass spontaneously into the quinoid

compounds, phenylfluorone,  $C_6H_5 \cdot C \begin{matrix} \diagup [1]C_6H_4 & [6] \\ \diagdown [1]C_6H_4 & \end{matrix} \begin{matrix} [6] \\ [4] \end{matrix} O$ , and phenylfluorime,

$C_6H_5 \cdot C \begin{matrix} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{matrix} \begin{matrix} O \\ =NH \end{matrix}$ , losing water. The last two compounds are the parent

substances of the fluorescein and rhodamine dyes (p. 550). Their solutions in alkalis or acids show strong fluorescence.

**Phenylfluorone**,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ , red needles, m.p.  $207^\circ$ , is obtained

from 4-aminophenylfluorone by elimination of the amino-group, and by condensation of 4-methoxyxanthone with phenyl magnesium bromide, and hydrolysing off the methoxy-group with aluminium chloride. It is insoluble in alkalis, but dissolves in acids. With alcoholic potash the solution loses its colour with formation of the carbinol (*Kehrmann*, Ann. 372, 293). 3- and 5-Hydroxy-phenyl-xanthydrol, m.p.  $170^\circ$  and  $162^\circ$ , respectively, correspond to 3- and 5-methoxy-xanthenes.

**Resorcinol-benzein**, 3-hydroxy-phenylfluorone-9,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{C}_6\text{H}_4(\text{OH}) \\ \text{C}_6\text{H}_4(:\text{O}) \end{array} \text{O}$ , forms brick-red crystals, m.p.  $333^\circ$ . It is obtained by the action of water on the reaction product of resorcinol and benzotrichloride, and by the action of zinc chloride on benzoic acid and resorcinol (*Cohn*, J. pr. [2], 48, 387; *Kehrmann*, Ber. 42, 873). It is also obtained by the action of concentrated sulphuric acid on benzyl alcohol and resorcinol at  $140\text{--}150^\circ$  (*Sen*, Am. 47, 1079). Dinitro-resorcinol-benzein, see *Cohn*, Ber. 28, 2064.

*vic*-Resorcinol-benzein, 2,2'-dihydroxy-phenyl-xanthydrol,

$\text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \begin{array}{l} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{array} \text{O}$ , is obtained from 2,2'-dihydroxy-xanthone and phenyl magnesium bromide (*Baeyer*, Ann. 372, 132).

**Hydroquinone-benzein**, 3,3'-dihydroxy-phenyl-xanthydrol, is obtained from 3,3'-dimethoxy-xanthone and phenyl magnesium bromide, followed by hydrolysis of the product (*Baeyer*, Ann. 372, 141), or by the condensation of benzaldehyde and hydroquinone with concentrated sulphuric acid, and oxidation of the xanthene derivative with ferric chloride (*Kehrmann*, Ann. 372, 301).

**Hydroxy-hydroquinone-benzein**, phenyl-trihydroxy-fluorone,

$\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{C}_6\text{H}_2(\text{OH})_3 \\ \text{C}_6\text{H}_2(\text{OH})_3 \end{array} \text{O}$ , is obtained by the action of benzaldehyde on hydroxy-hydroquinone in the presence of sulphuric acid (*Baeyer*, Ber. 37, 1171).

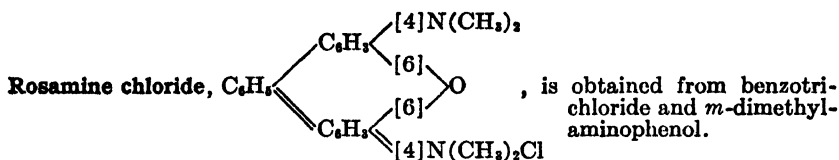
**Xylo-hydroquinone-benzeins** have been obtained by the condensation of xylo-hydroquinones with benzaldehyde in the presence of the corresponding quinones (*Kehrmann*, Ber. 45, 3346). **Thymol-benzein** (*Orndorff*, Am. 49, 818). **Pyrogallol-benzein**, etc. (*Sen*, Am. 47, 1079; J. Indian Chem. Soc. 1, 303).

### C. Aminoxy-triphenyl-carbinols

**4-Aminophenyl-fluorone**,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{C}_6\text{H}_4(\text{NH}_2) \\ \text{C}_6\text{H}_4(:\text{O}) \end{array} \text{O}$ , m.p.  $305^\circ$ , dark-red needles, is obtained in the form of its acetyl derivative by the condensation of N-acetyl-*m*-aminophenol with benzotrichloride, together with 4,4'-diacetaminophenylxanthydrol, m.p.  $248^\circ$  (*Kehrmann*, Ann. 372, 322).

**ROSAMINES**. Rosamines are alkyl compounds of 4-aminophenyl-fluorime (see below), which are obtained by the action of monoalkyl- and dialkyl-*m*-aminophenols on benzotrichloride. Although the benzeins formed with the phenols are only weak dyes, and their alkali salts are decomposed by atmospheric carbon dioxide, the hydrochlorides of the rosamines are red or violet dyes, showing great similarities to their closely-related rhodamines (p. 550) but with a more bluish-tinge and a fluorescence extending more into the red (*Heumann*, Ber. 22, 3001). The rosamines are also obtained by heating resorcinol-benzein with dimethyl- or diethyl-amine (see also pyronin).

The simplest rosamine, 4-aminophenyl-fluorime,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{C}_6\text{H}_4(\text{NH}_2) \\ \text{C}_6\text{H}_4(:\text{NH}_2\text{Cl}) \end{array} \text{O}$ , is obtained in the form of its red crystalline hydrochloride from 4,4'-diacetaminophenyl-xanthydrol (see above) by boiling with hydrochloric acid (*Kehrmann*, Ann. 372, 316).



Red and blue mordant dyes are obtained by the condensation of protocatechuic aldehyde with dialkyl-*m*-amino-phenols and with dialkylanilines: proto-red (leuco-compound,  $(\text{HO})_2\text{C}_6\text{H}_3\text{CH}[\text{C}_6\text{H}_4(\text{OH})\text{N}(\text{CH}_3)_2]_2$ ), and proto-blue (leuco-compound,  $(\text{HO})_2\text{C}_6\text{H}_3\text{CH}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2$ ) are examples (*Liebermann*, Ber. 36, 2913).

#### D. Aurines and Rosolic Acids

These are the oxygen-compounds corresponding to the rosanilines. The free *p,p',p''*-trihydroxytriphenylcarbinols are not known, but when separated from their salts they undergo an intramolecular anhydride or quinone formation.

These carbinol anhydrides or methylene-quinones (fuchsones, see p. 531) are yellow, and their alkali salts give red aqueous solutions. They are only incompletely fixed on plant fibres, and are only used in the form of their lakes in the paper industry.

**Aurine**, **pararosolic acid**, yellow corallin,  $(\text{HO}[4]\text{C}_6\text{H}_4)_2\text{C}:\text{C}_6\text{H}_4[4]:\text{O}$ , is obtained (1) by the decomposition of the diazonium salt of pararosaniline (p. 535) with water (*Fischer*, Ann. 194, 301); (2) by condensation of *p*-dihydroxy-benzophenone chloride with phenol (*Caro*, Ber. 11, 1350); (3) by condensation of phenol and formic acid with zinc chloride (*Nencki*, J. pr. [2], 23, 549); (4) by heating phenol (1 part), and anhydrous oxalic acid ( $\frac{2}{3}$  part) with sulphuric acid ( $\frac{1}{2}$  part) to 130–150° (*Zulkowsky*, Ann. 202, 185); (5) from carbon tetrachloride and phenol in the presence of zinc chloride (*Gomberg*, Am. 47, 198). For the by-products of the preparation of aurine by method 4, and their separation, see *Zulkowsky*, Ann. 194, 123; *Dale*, Ann. 196, 77; *Zulkowsky*, Mo. 16, 358).

Aurine forms dark-red crystals with a metallic lustre. It dissolves in alcohol and glacial acetic acid giving yellowish-red solutions, and decomposes when heated above 220°. It dissolves in alkalis with a magenta colour. It forms readily soluble, colourless compounds with alkali bisulphites; these are decomposed by acids or alkalis. With hydrogen chloride, aurine forms compounds which are decomposed by water. On reduction it is converted into *p,p',p''*-trihydroxy-triphenylmethane, or leucaurine (p. 539). On heating with water to 250° it breaks down into *p,p'*-dihydroxy-benzophenone and phenol.

When heated with aqueous ammonia to 150°, aurine is converted into pararosaniline. As an intermediate product, in which only one or two of the hydroxyl groups have been replaced by amino-groups, paeonin or red corallin is formed. In a similar way, with aniline, triphenyl-pararosaniline is formed, with azulin as an intermediate product. For isomeric acetylaurines, see *Herzig*, Mo. 17, 191. **Dimethylaurine**, m.p. 183–186°, is readily formed by methylation of aurine with diazomethane in ethereal suspension (*Herzig*, Mo. 29, 653).

*p,p',p''*-Trianisyl-carbinol,  $(\text{CH}_3\text{O}[4]\text{C}_6\text{H}_4)_3\text{COH}$ , m.p. 84°, colourless crystals, is formed by the action of lead dioxide on *p,p',p''*-trianisyl-methane (p. 539). Its OH group is even more reactive than that of triphenyl-carbinol (p. 525). It reacts with hydrocyanic acid to give trianisyl-acetonitrile. *o,o',o''*-, *m,m',m''*-, and *o,o',p*-Trianisyl-carbinol, m.p. 181°, 119°, and 110°, respectively, have been prepared by the action of *o*-, *m*-, and *p*-methoxybenzoic esters on the magnesium compounds of *o*- and *m*-iodoanisole (*Baeyer*, Ber. 35, 3024).

**3,3',3''-Trimethylaurine** is obtained from *o*-cresol and  $\text{CCl}_4$  by method 5.

**Rosolic acid**, the internal anhydride of *p,p',p''*-trihydroxy-diphenyl-*m*-tolyl-carbinol,  $\text{C}_{20}\text{H}_{10}\text{O}_5$ . Rosolic acid is obtained by similar methods to aurine, from rosaniline by boiling the diazonium chloride (*Graebe*, Ann. 179, 192), and by oxidation of a mixture of phenol and cresol with arsenic acid and sulphuric acid, when

the linking methane carbon atom is furnished by the methyl group of the cresol. Rosolic acid is reduced to the leucorosolic acid by warming with alcohol and zinc dust, and it can be re-formed from the leuco-compound by oxidation (Caro, Ber. 26, 254).

**Trihydroxy-aurine**,  $C_{19}H_{14}O_6$ , is obtained from catechol and formic acid with zinc chloride (Caro, Ber. 26, 255). **Resaurine**,  $C_{19}H_{14}O_6$ , is prepared in the same way from resorcinol. **Orcin-aurine**,  $C_{22}H_{14}O_6$  (Nencki, J. pr. [2], 25, 277; Schwarz, Ber. 13, 546). *o*-Amino-aurines, see Liebermann, Ber. 40, 3588.

**Eupittonic acid**, hexamethoxy-aurine,  $C_{19}H_8O_8(OCH_3)_6$ , obtained by the action of air on an alkaline solution of a mixture of pyrogallol dimethyl ether,  $C_6H_3(OH)(OCH_3)_2$ , and methyl-pyrogallol dimethyl ether,  $CH_3 \cdot C_6H_2(OH)(OCH_3)_2$ . It is an aurine, containing 6 methyl groups; forms orange-yellow crystals, melting at about 200° with decomp. It dissolves in alkalis with a deep blue colour, forming salts, which can be precipitated by adding excess alkali. (Hofmann, Ber. 12, 2216). Reichenbach (1835) observed the formation of the blue barium salt when fractions of beechwood tar were allowed to stand with baryta water, and called it *pillacal* (from *πύλλα*, tar, and *χάλλος*, beautiful). When heated with ammonia, eupittonic acid gives a *hexamethoxy-pararosaniline*, like aurine.

**Tetra- and hexamethoxy-triphenyl-carbinol**, see Kauffmann, Ber. 41, 4423.

### (f) and (g) Alcohols and Aldehydes of Triphenylmethane

Few of these are known. **Phenol-phthalol**,  $(HOC_6H_4)_2CHC_6H_4[2]CH_2OH$ , m.p. 190°, is obtained by the action of sodium amalgam on phenolphthalein (Baeyer, Ann. 202, 87).

**p-Diphenylmethyl-benzaldehyde**,  $(C_6H_5)_2CH[4]C_6H_4CHO$ , b.p. 190–195° (46 mm.), is produced by the condensation of terephthalaldehyde and benzene with concentrated sulphuric acid (Oppenheimer, Ber. 19, 2029). Dialdehydes have been prepared by the condensation of benzaldehyde, *m*- and *p*-nitrobenzaldehyde with vanillin and zinc chloride. **Benzal-divanillin**,  $C_6H_5CH[C_6H_4(OH)(OCH_3)-CHO]_2$ , m.p. 222°; *m*- and *p*-nitrobenzal-divanillin, m.p. 266° and 276° (decomp.) (Rogow, Ber. 36, 3975).

### (h) Carboxyl Derivatives of Triphenylmethane

**TRIPHENYLMETHANE CARBOXYLIC ACIDS** are prepared (1) by reduction of triphenylcarbinol carboxylic acids, and (2) from their nitriles, which are obtained by the action of aluminium chloride on cyanobenzal chloride (p. 382) and benzene.

**Triphenylmethane-*o*-carboxylic acid** (see phthaleins, p. 545),  $(C_6H_5)_2CH \cdot C_6H_4[2]COOH$ , m.p. 162°, is isomeric with triphenylacetic acid (p. 557). It is formed by reduction of diphenylphthalide (2), the lactone of triphenyl-carbinol-*o*-carboxylic acid (Baeyer, Ann. 202, 52), and from its nitrile. It is oxidised by chromic acid to diphenyl-phthalide, and when heated with barium hydroxide it breaks down into carbon dioxide and triphenylmethane. Sulphuric acid converts

it into **phenyl-anthrone**,  $C_6H_5CH \begin{matrix} \diagup C_6H_5 \\ \diagdown C_6H_5 \end{matrix} CO$ . ***o*-Cyano-triphenylmethane**,

$(C_6H_5)_2CH \cdot C_6H_4[2]CN$ , m.p. 89° (Drory, Ber. 24, 2572; preparation, see above).

***p,p'*-Tetramethyl-diamino-triphenylmethane-*o''*-carboxylic acid**,  $[(CH_3)_2N-4]C_6H_4)_2 \cdot CH \cdot C_6H_4[2]COOH$ , m.p. 200°, is obtained from tetramethyl-diaminodiphenyl-phthalide (p. 545) (Fischer, Ann. 206, 101).

**Triphenylmethane-*p*-carboxylic acid**, m.p. 161°, is obtained by heating *p*-carboxy-triphenylacetic acid above its melting point (Bistrzycki, Ber. 26, 3079). **Methyl-triphenylmethane-carboxylic acids**, see Hemilian, Ber. 16, 2364; 19, 3064; Gresly, Ann. 234, 242; Bauer, Mo. 53/54, 187.

**Triphenylmethane-2,2'-dicarboxylic acid**, m.p. 214–215°, has been obtained by oxidation of phenyl-*o*-tolyl-phthalin (Weiss, Mo. 53/54, 187). **Triphenylmethane-polycarboxylic acids** are obtained from triphenylmethane, oxalyl chloride, and aluminium chloride (Liebermann, Ber. 45, 1186).

**Hydroxy-triphenylmethane-carboxylic acids** are obtained by the reduction of hydroxy-triphenylcarbinol carboxylic acids. From the lactones of the corresponding hydroxy-triphenylcarbinol-*o*-carboxylic acids (p. 545), ***p*-hydroxy-**



triphenylmethane-*o*'-carboxylic acid,  $\text{HO}[4]\text{C}_6\text{H}_4\text{CH}(\text{C}_6\text{H}_5)_2\text{COOH}$ , m.p. 210° (Pechmann, Ber. 13, 1616) and *p,p'*-dihydroxy-triphenylmethane-*o*'-carboxylic acid, *phthalin*,  $[\text{HO}[4]\text{C}_6\text{H}_4]_2\text{CH}(\text{C}_6\text{H}_5)_2\text{COOH}$ , m.p. 225° (Baeyer, Ann. 202, 36, 153), are obtained. When treated with concentrated sulphuric acid they are converted into the corresponding hydroxy-phenylanthrone (*q.v.*).

Hydrofluoranic acid,  $\text{C}_6\text{H}_4\text{CH}(\text{C}_6\text{H}_4[2])\text{COOH}$ , m.p. 226-228°, is obtained in the reduction of fluorane, and tribromofluorane (p. 548). When distilled with lime, *xanthone* is formed, together with benzene. When distilled with baryta or soda-lime diphenylene-phenylmethane (*q.v.*) is formed (Meyer, Ber. 25, 3586). Fluorescein, *p,p'*-dihydroxy-hydrofluorane-carboxylic acid, is a reduction product of fluorescein (p. 548). *p,p'*-Dihydroxy-triphenylmethane-*m,m'*-dicarboxylic acid is produced by the condensation of benzaldehyde and salicylic acid by means of gaseous hydrogen chloride (Madsen, Ar. Pharm. 247, 65).

### (i) Carboxyl Derivatives of Triphenyl-Carbinol. Phthalide

The *o*-carboxyl-derivatives of this class are particularly important. They do not exist in the free state, but split off water, forming lactones, which may be regarded as diphenylated phthalides (see pp. 375, 524).

Diphenyl-phthalide, triphenylcarbinol-*o*-carboxylic lactone, incorrectly called "phthalophenone" (see p. 524),  $\text{C}_6\text{H}_4\text{CH}(\text{C}_6\text{H}_5)_2\text{COO}$ , m.p. 115°, is formed (1) by oxidation of triphenylmethane-*o*-carboxylic acid; (2) in small quantities by the action of mercury diphenyl on phthalyl chloride; (3) from phthalyl chloride and benzene in the presence of aluminium chloride; (4) by the action of phenyl magnesium bromide on phthalic anhydride (Bauer, Ber. 38, 240). The last two methods serve for the preparation of diphenyl-phthalide, which was at first regarded as *o*-phthalophenone (p. 524) until it was recognised to be a lactone, the parent substance of the phthaleins.

In the third method of preparation of diphenyl-phthalide, the phthalyl chloride can be replaced by phthalic anhydride. In this case *o*-benzoyl-benzoic acid is first formed, and is converted into diphenyl-phthalide by the further action of benzene and aluminium chloride. The acetyl derivative of *o*-benzoyl-benzoic acid is better for the preparation of diphenyl-phthalide than the acid itself (p. 524) (Pechmann, Ber. 14, 1865).

If diphenyl-phthalide is boiled with alkalis, it is converted into salts of triphenyl-carbinol-*o*-carboxylic acid, and from their solutions, acids regenerate diphenyl-phthalide. Triphenyl-carbinol-*o*-carboxylic acid is reduced by zinc dust in alkaline solution to triphenylmethane-*o*-carboxylic acid.

Anilide,  $\text{C}_6\text{H}_4\text{CH}(\text{C}_6\text{H}_5)_2\text{CON}(\text{C}_6\text{H}_5)_2$ , m.p. 189°, and phenylhydrazide,  $\text{C}_6\text{H}_4\text{CH}(\text{C}_6\text{H}_5)_2\text{CON}(\text{C}_6\text{H}_5)\text{NHC}_6\text{H}_5$ , m.p. 230° are obtained by boiling diphenyl-phthalide with aniline hydrochloride (Fischer, Ber. 27, 2793) and with phenylhydrazine (Meyer, Ber. 26, 1273), respectively.

Dithio-diphenyl-phthalide,  $\text{C}_6\text{H}_4\text{CH}(\text{C}_6\text{H}_5)_2\text{CSS}$ , is obtained by the action of

phosphorus pentasulphide on diphenyl-phthalide (Meyer, C. 1900, II, 575).

Nitration of diphenyl-phthalide gives two dinitro-diphenyl-phthalides, from which two diamino-diphenyl-phthalides may be obtained (Baeyer, Ann. 202, 66).

*p,p'*-Tetramethyl-diamino-diphenyl-phthalide,  $C_6H_4 \begin{matrix} \swarrow [1]C:[C_6H_4[4]N(CH_3)_2] \\ \searrow [2]COO \end{matrix}$ ,

m.p. 190°, is obtained by condensation of phthalic anhydride and dimethyl-aniline with zinc chloride. If phthalyl chloride is used in place of the anhydride, a second compound is also formed, called phthalyl-green; it is a derivative of anthracene, and is used industrially as a substitute for malachite green. Its formation is due to the presence of phthalylene-tetrachloride (p. 385) in phthalyl chloride (Haller, C.r., 125, 1153; Bull. soc. ind. Mulhouse, 72, 268). The ester of the colourless tetramethyl-diamino-diphenyl-phthalide forms quinoid salts with an intensely blue colour when treated with acids.

Triphenyl-carbinol-*m*-carboxylic acid, m.p. 161°, and triphenyl-carbinol-*p*-carboxylic acid, m.p. 200°, are formed by the oxidation of diphenyl-*m*-tolylmethane and diphenyl-*p*-tolylmethane or diphenyl-*p*-tolyl-carbinol with chromic acid. The latter can also be made by the oxidation of *p*-diphenylmethyl-benzaldehyde (p. 543) and triphenylmethane-*p*-carboxylic acid (p. 543; Hemilian, Ber. 16, 2369; Fischer, Ber. 26, 3081; Bistrzycki, Ber. 37, 657).

Phenyl-*p*-tolylphthalide is obtained from acetyl-*o*-benzoyl-benzoic acid and toluene, benzoyl-*o*-benzoyl chloride and toluene, tolyl-*o*-benzoyl chloride and benzene with aluminum chloride (Pechmann, Ber. 14, 1867; Guyot, Bull. [3], 15, 133). Phenyl-*o*-tolyl-phthalide, m.p. 120°, is obtained from *o*-tolyl-magnesium bromide and *o*-benzoyl-benzoic acid (Weiss, Mo. 53/54, 187). Isomeric methylated diphenyl-phthalides are obtained by oxidation of diphenyl-*m*- and -*p*-xylyl-methanes (p. 526). Ditolyl-phthalide, m.p. 116° (Haller, C.r. 125, 1153; Lim-

pricht, Ann. 299, 286). Bidiphenyl-*o*-phthalide,  $C_6H_4 \begin{matrix} \swarrow [1]CO \cdot O \\ \searrow [2]C \equiv (C_6H_4 \cdot C_6H_5)_2 \end{matrix}$ ,  
(see Pawlewski, Ber. 28, 513).

### Carboxyl Derivatives of the Hydroxy-triphenyl-carbinols

The derivatives of the phthalides with two phenol radicals are of particular interest. They are the phthaleins, discovered by Baeyer in 1871, and dyes of technical importance belong to this series. Between diphenyl-phthalide and the phthaleins lie the diphenylphthalides which are hydroxylated in only one benzene nucleus.

Phenyl-phenolphthalide,  $C_6H_4 \begin{matrix} \swarrow [1]C(C_6H_5)C_6H_4OH \\ \searrow [2]COO \end{matrix}$ , m.p. 167°, is

obtained from *o*-benzoyl-benzoic acid, phenol, and concentrated sulphuric acid (Baeyer, Ann. 354, 171).

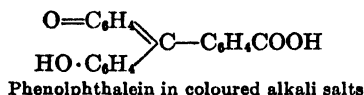
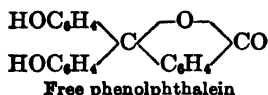
In a similar way the following are obtained: resorcy-phenyl-phthalide, m.p. 199°; catechol-phenyl-phthalide, m.p. 161°; hydroquinone-phenyl-phthalide, m.p. 247°; pyrogallol-phenyl-phthalide, m.p. 189° (Baeyer, Ann. 372, 91). The polyhydroxy-diphenyl-phthalides, if they are *p*-substituted, dissolve in alkalis giving a red solution, the lactone ring being broken and *p*-quinoid salts formed (cf. phenolphthalein).

The phthaleins are formed by the condensation of phthalic anhydride (1 mol.) and phenols (2 mols.) with concentrated sulphuric acid, or zinc chloride at 120° (at higher temperatures hydroxy-anthraquinones are chiefly formed) or anhydrous oxalic acid at 115°. Phthaleins formed from di- and polyhydric phenols usually lose water from two phenolic hydroxyl groups, which are attached to different benzene nuclei, forming anhydrides (Baeyer, Ann. 212, 347). In the case of the condensation of phthalic anhydride and phenol, the

anhydride of *o,o'*-dihydroxy-diphenyl-phthalide, or fluorane is formed in addition to *p,p'*-dihydroxy-diphenyl-phthalide, or *phenolphthalein*. These phthalein anhydrides, of which the simplest is *fluorane*, contain the xanthone ring.

The free phthaleins are usually colourless, crystalline substances, which dissolve in dilute alkalis forming highly coloured solutions. Acids, even carbon dioxide, will liberate the phthaleins from their alkaline solutions. Addition of concentrated alkali causes the colour to disappear, but it returns on dilution with water.

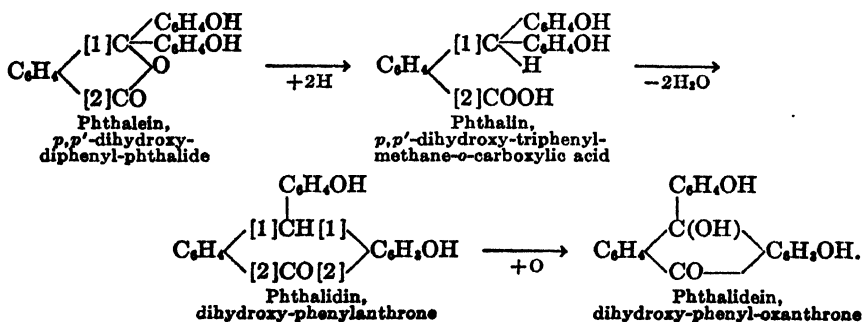
To show the similarity of the phthaleins to the aurines and rosanilines, as far as formula is concerned, it is assumed that the free, colourless phthaleins contain a lactone ring, but in the coloured solutions of their alkali salts the lactone ring disappears, and the methane carbon atom and an oxygen atom form a quinone structure with one of the benzene nuclei:



In agreement with this view, *m,m'*-dihydroxy-ditolyl-phthalide gives a colourless solution with alkalis, because the non-existence of *m*-quinones does not allow of an analogous formulation for them. Also, in confirmation of the quinoid formula, there are the reactions in which phenolphthalein and its derivatives couple with diazonium salts (*Schestakow*, Ber. 47, 331; *Oddo*, Ber. 47, 967; *Consonno*, Gazz. 51, I, 60; *Bassett*, J. 123, 1291). It is interesting to note that phenolphthalein, when treated with a Grignard reagent, shows no evolution of methane, and other formulae have been put forward to explain this fact (*Oddo*, Gazz. 42, II, 204). By the addition of a considerable excess of alkali the red solution of phenolphthalein is decolourised with formation of salts of the carbinol,  $\text{NaO}_2\text{CC}_6\text{H}_4\cdot\text{C}(\text{OH})(\text{C}_6\text{H}_4\text{ONa})_2$  (*Green*, Proc. 20, 50). It is noteworthy that acylation and alkylation of phenolphthalein, even in alkaline solution, leads to the formation of lactonic esters and ethers.

When reduced, the phenolphthaleins are converted into hydroxy-triphenylmethane-carboxylic acids, called *phthalins* (p. 543), which, on treatment with concentrated sulphuric acid, give hydroxy-phenylanthrone derivatives, called *phthalidines*. When oxidised the phthalidines are converted into *phthalideins* or hydroxyphenyloxanthrone derivatives.

The following scheme shows these relationships in the case of phenolphthalein:



**Phenolphthalein**, *p,p'*-phthalein, *p,p'*-dihydroxy-diphenyl-phthalide,  $C_{20}H_{14}O_4$  (constitution, see above), m.p.  $250^\circ$ , crystallises from alcohol in colourless, crystalline crusts. It is almost insoluble in water, but dissolves in alkalis with a magenta red colour. It is used as an indicator in alkalimetry, particularly for the estimation of carbonate by baryta. It is obtained by the action of nitrous acid on *p,p'*-diaminodiphenyl-phthalide, from the corresponding phthalin (see above) by atmospheric oxidation in alkaline solution, or by oxidation with potassium ferricyanide or permanganate, and by condensation of phthalic anhydride and phenol with concentrated sulphuric acid or tin chloride at  $115-120^\circ$ . *o,o'*-Dihydroxy-diphenyl-phthalide-anhydride, or fluorane, is formed as a by-product, but is insoluble in alkali (*Baeyer*, Ann. 202, 68). In the commercial preparation of phenolphthalein an *iso*-phenolphthalein is also formed as a by-product. It is a derivative of an *o,p'*-diphenol-phthalide, and can also be prepared from *o*-hydroxy-benzoyl-*o*-benzoic acid (*q.v.*), phenol, and a good excess of condensing agent (*Orndorff*, Am. 46, 2483). When boiled with caustic soda and zinc dust, phenolphthalein is reduced to the phthalin (see above and p. 543), and when fused with potash it is broken down into dihydroxy-benzophenone and benzoic acid.

**Derivatives of phenolphthalein.**—**Diacetyl-phenolphthalein**, m.p.  $143^\circ$ ; **di-benzoyl-phenolphthalein**, m.p.  $169^\circ$  (*Bistrzycki*, Ber. 29, 131). **Phenolphthalein**

**methyl ester**,  $CH_3OOC \cdot C_6H_4 \cdot C \begin{smallmatrix} \diagup C_6H_4 : O \\ \diagdown C_6H_4 \cdot OH \end{smallmatrix}$ , m.p.  $127-130^\circ$ , orange-red needles,

is obtained by esterifying phenolphthalein with methyl-alcoholic sulphuric acid. It dissolves in alkalis with a violet-red colour; and is readily hydrolysed to phenolphthalein (*Meyer*, Ber. 40, 3484; *Green*, Ber. 40, 3726). The lactoid phenolphthalein-mono- and -di-methyl ethers, m.p.  $149^\circ$  and  $100^\circ$ , respectively, have been obtained by alkylation of phenolphthalein in alkaline solution (*Green*, Ber. 40, 3729). The latter can be obtained synthetically from phthalic anhydride, anisole and aluminium chloride (*Grandi*, Gazz. 26, I, 222). **Phenol-**

**phthalein-anilide**,  $C_6H_4 \begin{smallmatrix} \diagup [1]C = (C_6H_4 \cdot OH)_2 \\ \diagdown [2]CONC_6H_5 \end{smallmatrix}$ , m.p.  $279^\circ$  (*Albert*, Ber. 26, 3077).

**Phenolphthalein-oxime**,  $(C_{20}H_{14}O_3) : NOH$ , yellow crystalline powder, m.p.  $212^\circ$  (decomp.), is obtained by the action of hydroxylamine on an alkaline solution of phenolphthalein. When treated with dimethyl sulphate and alkali it gives a **trimethyl derivative**, and when acted upon by phenyl-diazonium chloride a mono-diazo-compound, which gives a diacetyl derivative. On boiling with dilute sulphuric acid the oxime breaks down into *p*-hydroxy-*o*-benzoyl-benzoic acid and *p*-aminophenol (*Meyer*, Ber. 42, 2825).

By the introduction of halogen into the nucleus of phenolphthalein, the intensity of colour decreases. This fact has been explained as due to a displacement of the equilibrium in favour of the lactoid form in solution (*Thiel*, Z. physikal. Chem. 100, 479).

**Tetrachloro-phenolphthalein**,  $C_{20}H_{10}Cl_4O_4$ , m.p. above  $300^\circ$  (*Orndorff*, Am. 41, 349). **Tetrabromo-phenolphthalein**, m.p.  $220-230^\circ$  (decomp.). **Tetraiodo-phenolphthalein** is used under the name of nosphen as a substitute for iodoform. For other halogeno-phenolphthaleins, see *Thiel*, Ber. 55, 1312; *Greenbaum*, Am. Pharm. 100, 374; *Blicke*, Am. 51, 1865. **Tetrabromo-phenolphthalein oxime** see *Friedländer*, Ber. 26, 2260; *Meyer*, Mo. 21, 263. Quinoid **tetrabromo-phenolphthalein-mono- and -di-ethyl ethers**, see *Meyer*, Ber. 40, 1437.

*m,m'*-Dihydroxy-*p,p'*-ditolyl-phthalide, m.p.  $206^\circ$ , see *Baeyer*, Ann. 354, 185.

**Phenol-sulphone-phthalein**,  $C_6H_4 \begin{smallmatrix} \diagup C = (C_6H_4 \cdot OH)_2 \\ \diagdown \begin{smallmatrix} O \\ SO_2 \end{smallmatrix} \end{smallmatrix}$ , is obtained by the action of

*o*-sulphobenzoyl chloride on phenol at  $135-140^\circ$ . Like phenolphthalein, it forms colourless lactone derivatives and coloured quinone compounds (*Orndorff*, Am. 45, 486).

**Fluorane**, *o,o'*-phenolphthalein-anhydride,  $C_6H_4 \begin{smallmatrix} \diagup [1]C \begin{smallmatrix} \diagup C_6H_4 [2] \\ \diagdown C_6H_4 [2] \end{smallmatrix} \\ \diagdown [2]COO \end{smallmatrix}$ , m.p.

$173-175^\circ$ , is obtained together with *p,p'*-phenolphthalein in the condensation of

phthalic anhydride and phenol, and by dry distillation of copper phthalate (*Ekeley*, *Am.* 52, 3003). When reduced, fluorane gives hydrofluoranic acid (p. 544), and is converted by distillation with zinc dust into diphenylene-phenylmethane

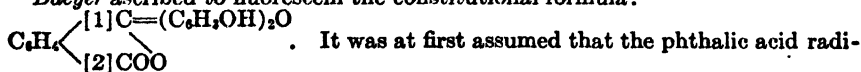
(*Meyer*, *Ber.* 25, 3586). The anil,  $C_6H_5 \begin{matrix} \swarrow [1]C=(C_6H_5)_2O \\ \searrow [2]CON \cdot C_6H_5 \end{matrix}$ , melts at 242° (*Albert*, *Ber.* 27, 2793). 6-Hydroxy-fluorane, m.p. 181°, is obtained from 2,4-dihydroxy-benzoyl-benzoic acid, phenol, and concentrated sulphuric acid. For other hydroxy- and polyhydroxy-fluoranes, see *Ghatak*, *J. Indian Chem. Soc.* 6, 465. Tribromo-fluorane,  $C_{20}H_{12}Br_3O_5$ , m.p. 298–300°, is obtained by the action of phosphorus pentabromide on fluorescein, and gives hydrofluoranic acid when reduced with alcoholic soda and zinc dust (*Meyer*, *Ber.* 25, 1388). Tetra-bromo-fluorane, *Pratt*, *Am.* 41, 1289. For nitrofluoranes see *Meyer*, *Ber.* 31, 1739; *Gattermann*, *Ber.* 32, 1131; *Meyer*, *Ber.* 32, 2108. 3,6-Dimethyl-fluorane, m.p. 213°. 2,7-Dimethyl-fluorane, m.p. 246°, see *Copisarow*, *J.* 117, 209.

Fluoresceins are the *o*-dihydroxy-phenolphthalein anhydrides, which are obtained by condensation of phthalic anhydrides with resorcinol, and are characterised by their beautiful fluorescence, especially in alkaline solutions (*Baeyer*, *Ann.* 183, 1).

Phthalic anhydride can be replaced by the anhydrides of aliphatic dicarboxylic acids. Succinic, maleic, and citraconic anhydrides will condense with resorcinol to give the corresponding fluoresceins. Pyromellitic and mellitic acids and their anhydrides also combine with resorcinol to give dyes similar to fluorescein, which contain 1, 2, or 3 xanthy groups (*Silberrad*, *Proc.* 22, 251; *J.* 89, 1787). See also *o*-sulphobenzoic acid (p. 332), and naphthalic acid (*Pechmann*, *Ber.* 15, 883; *Burckhardt*, *Ber.* 18, 2864; *Hewitt*, *J.* 59, 301; *J.* 63, 677; *Ber.* 29, 2824). Hydroquinone-succinein; pyrogallol-succinein.

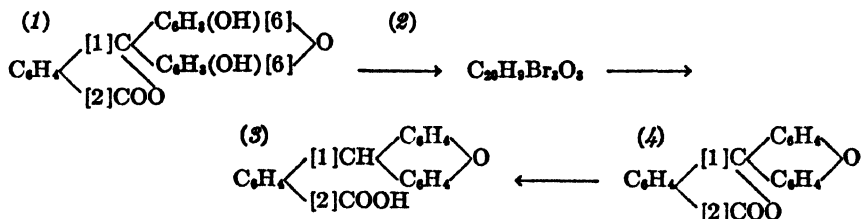
Fluorescein,  $C_{20}H_{12}O_5$ , is obtained by heating phthalic anhydride (2 parts) with resorcinol (7 parts) by themselves to 200°, or with anhydrous oxalic acid to 110–117° (*Anschütz*, *Ber.* 17, 1079). When precipitated from alkaline solution it forms yellowish-red flocks with the composition  $C_{20}H_{14}O_6$ , which easily lose water and pass into  $C_{20}H_{12}O_5$ . It is obtained as a dark red powder from its solution in alcohol, which is yellowish-red with a green fluorescence. The various forms of fluorescein are possibly due to the varying proportions of quinoid and lactoid forms present (*Liebig*, *J. pr.* [2], 86, 472; *Orndorff*, *J.* 49, 1272). The alkaline solution is dark red, but becomes yellow when diluted, and then shows a beautiful green fluorescence. When reduced fluorescein gives fluoresein (p. 544). With phosphorus pentachloride it is converted into *fluorescein chloride*, *p,p'*-dichloro-fluorane (see rhodamines, p. 550), which, on treatment with alcoholic potassium hydrosulphide gives *thiofluorescein*,  $C_8H_4O_2:(C_6H_5SH)_2:O$  (*Gattermann*, *Ber.* 32, 1127).

*Baeyer* ascribed to fluorescein the constitutional formula:



replaced the two *m*-hydrogen atoms in the resorcinol molecule. *Meyer* proved that fluorescein was a dihydroxy-derivative of *o*-phenolphthalein-anhydride, and hence gave it the name fluorane (p. 547); he also showed that the phthalic acid radical was in the *o*-position to one of the hydroxyl groups of the resorcinol molecule, and that anhydride formation took place between these two hydroxyl groups. *R. Meyer* converted fluorescein (1) into tribromo-fluorane (2) with phosphorus pentabromide, which, like fluorane (4), itself, gave hydrofluoranic acid (3) on reduction. Fluorescein and fluorane contain a ring closely related to the xan-

thone ring, a fact which is confirmed by the formation of an oxonium salt with hydrochloric acid (*Fischer*, J. pr. [2], 104, 123); hydrofluoric acid can be broken down into xanthone and benzene:



The intense colour of fluorescein itself led *Bernthsen* and others to ascribe a quinoid constitution to free fluorescein and its coloured derivatives (see phenolphthalein). The ready solubility of fluorescein in sodium bicarbonate, and its esterification with alcohol and sulphuric acid is in agreement with the existence of a free carboxyl group in the molecule. The colourless derivatives were supposed to originate from a lactone form of fluorescein. Fluorescein and its coloured derivatives are thus brought into relationship with the aurines and rosanilines.

If fluorescein is fused with caustic soda it breaks down into resorcinol and monoresorcinolphthalein or dihydroxy-benzoyl-benzoic acid. When treated with bromine in glacial acetic acid, the latter gives dibromo-dihydroxy-benzoyl-benzoic acid, which can also be obtained from eosin, and with fuming sulphuric acid is converted into dibromo-xanthopurpurin. It follows that monoresorcinol-phthalein is 2,4-dihydroxy-*o*-benzoyl-benzoic acid, for if it were the 2,6-compound it would be impossible for an anthraquinone condensation to take place (*Heller*, Ber. 28, 314; *Meyer*, Ber. 29, 2623).

*Derivatives of fluorescein.*—**Fluorescein-anilide** and **phenyl-hydrazide**,  $\text{C}_6\text{H}_5 \begin{array}{l} \swarrow \text{C}(\text{C}_{12}\text{H}_9\text{O}_2) \\ \searrow \text{CONC}_6\text{H}_5 \end{array}$  and  $\text{C}_6\text{H}_5 \begin{array}{l} \swarrow \text{C}(\text{C}_{12}\text{H}_9\text{O}_2) \\ \searrow \text{CON-NHC}_6\text{H}_5 \end{array}$ , are obtained by heating fluorescein with aniline and phenylhydrazine, respectively. They form colourless crystals. The anhydride gives a *dimethyl-ether*, m.p. 207° (*Fischer*, Ber. 28, 396; *Gattermann*, Ber. 32, 1133).

**Fluorescein-carboxylic-acid methyl ester**,  $\text{CH}_3\text{OOC}[2]\text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \swarrow \text{C}_6\text{H}_5 \\ \searrow \text{C}_6\text{H}_5 \end{array} \begin{array}{l} \nearrow \text{OH} \\ \searrow \text{O} \end{array}$ , m.p. 281–282°, crystals with a green lustre, is obtained by the esterification of fluorescein with sulphuric acid and methyl alcohol (*Feuerstein*, Ber. 34, 2641), or by the action of dimethyl sulphate on sodio-fluorescein (*Liebig*, J. pr. [2], 88, 26; *Fischer*, Ber. 46, 1951). Further methylation with dimethyl sulphate in nitrobenzene solution gives the orange-red **fluorescein-dimethyl-ether ester**,  $\text{CH}_3\text{OOC}\text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \swarrow \text{C}_6\text{H}_5\text{OCH}_3 \\ \searrow \text{C}_6\text{H}_5\text{OCH}_3 \end{array} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array}$ , m.p. 208° (*Fischer*, loc. cit.), and the colourless

**lactoid dimethyl-ether**,  $\text{C}_6\text{H}_5 \begin{array}{l} \swarrow \text{C} \begin{array}{l} \nearrow \text{C}_6\text{H}_5(\text{OCH}_3) \\ \searrow \text{C}_6\text{H}_5(\text{OCH}_3) \end{array} \text{COO} \end{array}$ , apparently formed by isomeri-

sation. The latter melts at 198°, and can also be obtained from its anilide (see above) by heating with concentrated sulphuric acid. From the dimethyl-ether ester, m.p. 208°, the colourless **fluorescein-lactone-methyl ether** m.p. 265–266°, is formed by hydrolysis (*Fischer*, loc. cit.). The dimethyl ether, m.p. 198°, gives on further esterification with methyl alcohol and hydrogen chloride, the *trimethyl ether* of dihydroxy-xanthidol-carboxylic acid, which possesses strongly basic properties. With acids it gives highly coloured salts which are soluble in water without hydrolysis.

*Substituted fluoresceins.*—While fluorescein itself is of no value as a dye, dye-stuffs of great beauty can be obtained from it by introducing halogen and nitro-groups. Starting from fluorescein, the substitution takes place in the resorcinol

radical (Ger. Pat. 108,838). The introduction of halogen results in a displacement of the absorption bands to the red end of the spectrum. The displacement is approximately proportional to the number of halogen atoms introduced (Orndorff, Am. 36, 680). The halogenated fluoresceins exist in two forms, one colourless (lactoid) and the other coloured (quinoid). They give deep red fluorescent solutions with alkalis.

**Eosin**, *tetrabromofluorescein*,  $C_{20}H_5Br_4O_6$ , is obtained by the action of bromine in glacial acetic acid on fluorescein. It crystallises from alcohol in yellowish-red crystals, which can be converted into a colourless form through the diacetate. If the colourless form is dissolved in alkali and acetic acid is added, the coloured form is precipitated (Orndorff, Am. 49, 1272). The water soluble eosin of commerce is the potassium of sodium salt. It dyes wool and silk a beautiful red, and in the case of silk the colour is fluorescent.

**Erythrosin**, *tetraiodofluorescein*,  $C_{20}H_5O_6I_4$ , crystallises with 1 mol. of water which is very firmly held. For its constitution, see Holmes, Am. 49, 1594.

**Safrosin**, *eosin scarlet*, *dibromo-dinitrofluorescein*,  $C_{20}H_5Br_2(NO_2)_2O_6$ , is obtained by the action of bromine on dinitrofluorescein, or by the action of nitric acid on di- or tetrabromofluorescein (Baeyer, Ann. 202, 68). For **dinitrofluorescein yellow**, obtained by the action of ammonia on dinitrofluorescein, see Reverdin, Ber. 30, 333. For further nitrofluoresceins, see Liebig, J. pr. [2], 86, 472.

In order to obtain chloro-substituted fluoresceins in which the substitution has taken place in the phthalic acid radical, chlorinated phthalic anhydrides are condensed with resorcinol (Noelting). From brominated fluoresceins, fluoresceins brominated and iodinated at the same time in the resorcinol radical are obtained:

**Phloxine**, *tetrabromo-dichloro-* and *tetrabromo-tetrachloro-fluorescein*,  $C_{20}H_4Cl_4Br_4O_6$ ; *rose bengal*, *tetraiodo-tetrachloro-fluorescein* (Orndorff, Am. 36, 680; Pratt, Am. 40, 236; Am. 41, 1293).

*Catechol* (Meyer, Ber. 40, 1442), *hydroquinone*, *orcinol* (Orndorff, Am. 36, 1201), *hydroxyhydroquinone*, *pyrogallol*, and *phloroglucinol* have also been condensed with phthalic anhydride.

**Hydroquinone-phthalein**, m.p.  $226^\circ$ , is obtained from hydroquinone and phthalic anhydride, and from fluorane (p. 547) by conversion into 2,7-dinitrofluorane, diaminofluorane, and treatment of the latter with nitrous acid (Meyer, Ber. 28, 2959; 31, 1743). It is not fluorescent, and differs from fluorescein in its colour. In its properties it resembles phenolphthalein much more closely (Meyer, Ber. 36, 2949). It dissolves in alkalis with a violet colour, which is not very stable; apparently the xanthone ring breaks and *o*-quinoid salts are formed (cf. hydroquinonebenzein; Baeyer, Ann. 372, 133). For esters of hydroquinone-phthalein, see Kehrman, Ann. 372, 298. By condensation of phthalic anhydride with orcinol, three *orcinolphthaleins* are obtained. Only that compound which has 2 hydroxyl groups in the para-position to the phthalic acid radical, acts in a completely analogous manner to fluorescein (Meyer, Ber. 29, 2630).

**Pyrogallolphthalein**, *gallein*,  $HOOC[2]C_6H_4C \begin{matrix} \nearrow C_6H_3(OH)_2 \\ \searrow C_6H_2(OH)_3 \end{matrix} \begin{matrix} \nearrow O \\ \searrow O \end{matrix}$ , is formed by heating pyrogallol with phthalic anhydride to  $200^\circ$ . Crystals with a green lustre are formed, which dissolve in alcohol and in alkalis with a dark-red colour. With excess of alkali the solution becomes blue. Concentrated sulphuric acid converts gallein into *coerulein*, a green anthracene dye which is fast to light (Buchka, Ann. 209, 249; Orndorff, Am. 23, 425; 26, 97). **Tetrachlorogallein** see Orndorff, Am. 42, 183.

**Hydroxyhydroquinonephthalein** is similar to the isomeric gallein, and in contrast to *phloroglucinolphthalein* which does not contain the hydroxyl group in the ortho-position, is a useful mordant dye for cotton. Hydroxyhydroquinonephthalein, like gallein, is converted by concentrated sulphuric acid into an anthracene derivative, *violetin*; Hydroxyhydroquinone reacts like resorcinol with many other 1,2-dicarboxylic acid anhydrides, with phthalein formation (Thiele, Ber. 34, 2617, 2637; Liebermann, Ber. 35, 1782; 36, 1070).

The phthaleins obtained from *m*-aminophenols and their derivatives are called **rhodamines**. Like fluorescein they are beautiful red dyes. The simplest rhodamine is obtained by heating phthalic anhydride with *m*-aminophenol hydrochloride and concentrated sulphuric acid to  $190^\circ$  (Ger. Pat. 44,002; Noelting, Ber. 38, 3516; 39, 2744).

More highly coloured than the hydrochloride of this simplest rhodamine are the **alkylated rhodamines**. They are obtained (1) by heating the simple rhodamine hydrochloride with alkyl iodides; (2) more easily by the condensation of alkylated and phenylated *m*-aminophenols with phthalic anhydride (Ger. Pats. 44,002 and 48,731; *Piutti*, Ber. 31, 1327; *Noelling*, C. 1898, II, 1049); (3) by heating *fluorescein chloride*, m.p. 252°, the product obtained by the action of phosphorus pentachloride on fluorescein, with dialkylamines (Ger. Pats. 48,367 and 48,980). *Anisoline*, an alkyl ether of rhodamine (?) see *Monnet*, Bull. [3], 7, 523. *Succin-rhodamine*, obtained from succinic anhydride and *m*-aminophenol, see Ger. Pat. 51,983.

**Disalicylic-phthalide**,  $C_6H_4 \begin{matrix} \swarrow [1]C[C_6H_4(OH)COOH]_2 \\ \searrow [2]COO \end{matrix}$ , m.p. 276° (decomp.), is

obtained, together with phthaloyl-salicylic acid (p. 523), from phthalic anhydride, ethyl salicylate and aluminium chloride (*Limpricht*, Ann. 303, 280).

**2 A.** The ring system of diphenyl and triphenylmethane are combined in **tri-diphenyl-methane**,  $HC \left( \text{—} \langle \text{C}_6\text{H}_5 \rangle \text{—} \right)_3$ , m.p. 241–242°. It is formed by the action of diphenylmethyl magnesium bromide on *bis*-diphenyl-ketone (*Schmidlin*, Ber. 45, 3178; *Schlenk*, Ber. 46, 1476). It is also produced from the corresponding tri-diphenyl-chloromethane (m.p. 200°) by the action of concentrated sulphuric acid in alcohol (*Schmidlin*, Ber. 45, 3189). The transformation of tri-diphenyl-chloromethane into the free radical tri-diphenyl-methyl on heating its benzene solution with copper powder (*Schlenk*, Ann. 372, 2) is remarkable.

**2 B.** *p*-Phenylene-*bis*-diphenylmethane,  $C_6H_4 \begin{matrix} \swarrow CH(C_6H_5)_2 \\ \searrow CH(C_6H_5)_2 \end{matrix}$ , m.p. 172°, ob-

tained from the corresponding glycol (*q.v.*) by reduction with zinc and acetic acid. Derivatives of this hydrocarbon have been obtained by introducing the  $CH(C_6H_5)_2$ — group into quinones and quinoid substances by means of diphenylcarbinol (p. 513). **Benzoquinone-*bis*-diphenylmethane**,  $C_6H_2O_2[CH(C_6H_5)_2]_2$ , m.p. 250°. **Benzoquinone-*bis*-(tetramethyl-diamino-diphenylmethane)**, m.p. 245°, is obtained by warming quinone with tetramethyl-diamino-diphenylcarbinol in alcoholic solution (*Möhlau*, Ber. 32, 2146).

*p*-Phenylene-*bis*-diphenylcarbinol,  $(C_6H_5)_2C(OH)[1]C_6H_4[4]C(OH)(C_6H_5)_2$ , m.p. 169°, has been obtained from ethyl terephthalate and phenyl magnesium bromide. The benzene solution of the bromide,  $(C_6H_5)_2CBrC_6H_4CBr(C_6H_5)_2$ , gives **tetraphenyl-dimethylene-quinone**,  $(C_6H_5)_2C:C_6H_4:C(C_6H_5)_2$ , when boiled with silver. This substance forms orange-red needles, m.p. 239–242°. It adds on bromine with decolorisation, liberates iodine from hydriodic acid, and resembles the methylene-quinones (p. 340) (*Thiele*, Ber. 37, 1463; *Flürscheim*, Ber. 41, 2746). Tetraphenyl-methylene-quinones are also formed by the condensation of 2 mols. of diphenylketene with 1 mol. of quinone, 2 mols. of carbon dioxide being split off from the first-formed  $\beta$ -dilactones (p. 554). If glycol is treated with aniline salts, or phenol in glacial acetic acid, *p,p'*-diamino- and *p,p'*-dihydroxy-hexaphenyl-*p*-xylene,  $H_2NC_6H_4 \cdot C(C_6H_5)_2C_6H_4C(C_6H_5)_2C_6H_4NH_2$ , m.p. 358°, and  $HO C_6H_4C(C_6H_5)_2C_6H_4C(C_6H_5)_2C_6H_4OH$ , m.p. 304°, respectively, are formed (*Ullmann*, Ber. 37, 2001).

### 3. TETRAPHENYLMETHANE GROUP

**Tetraphenylmethane**,  $C(C_6H_5)_4$ , m.p. 282°, b.p. 431° (sublimes), has been obtained from the diazonium sulphate of *p*-amino-tetraphenylmethane by boiling with alcohol. It is also formed in small quantities by heating triphenylmethane-azobenzene (p. 530) to 100° (*Gomberg*, Ber. 36, 1090), and by the action of phenyl magnesium chloride on triphenylchloromethane or triphenylcarbinol methyl ether (*Gomberg*, Ber. 39, 1463; *Am.* 39, 2009). *p*-Amino- and *p*-hydroxy-tetraphenylmethane,  $NH_2[4]C_6H_4C(C_6H_5)_3$  and  $HO[4]C_6H_4C(C_6H_5)_3$ , m.p. 245° and 282°, respectively, are easily obtained from triphenylcarbinol in glacial acetic acid by heating with aniline hydrochloride, and phenol and concentrated sulphuric acid, respectively (*Baeyer*, Ber. 35, 3018; *Ullmann*, Ber. 36, 407; *Bistrzycki*, Ber. 37, 659; *Zincke*, Ann. 363, 284).



*p*-Diphenylmethyl-tetraphenylmethane,  $(C_6H_5)_2CH[4]C_6H_5C(C_6H_5)_3$ , m.p.  $231^\circ$ , is obtained by reduction of triphenylcarbinol or its chloride with zinc and stannous chloride, hydrochloric acid and acetic acid, and also by the action of hydrochloric acid on hexaphenylethane and triphenylmethyl (p. 575) (*Tshitshibabin*, Ber. 37, 4709). It has also been obtained synthetically from *p*-benzoyl-triphenylmethane,  $C_6H_5COC_6H_4CH(C_6H_5)_2$ , m.p.  $166^\circ$  (*Tshitshibabin*, Ber. 41, 2421).

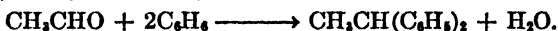
#### 4. HOMOLOGOUS DI- AND POLY-PHENYL PARAFFINS

Homologous series are derived from diphenylmethane. Apart from substitution in the benzene nuclei, H atoms of the methylene radicals may be replaced by alkyl groups, giving rise to compounds such as diphenylmethyl-, diphenyldimethyl-, diphenylethyl-, diphenylpropyl-methane, *etc.* These are known generally as *gem*-diphenyl paraffins. Secondly, new carbon atoms may be introduced between the two benzene radicals giving rise to compounds such as  $\omega,\omega$ -diphenylethane, or dibenzyl,  $\omega,\omega$ -diphenylpropane,  $\omega,\omega$ -diphenylbutane,  $\omega,\omega$ -diphenylpentane, *etc.*

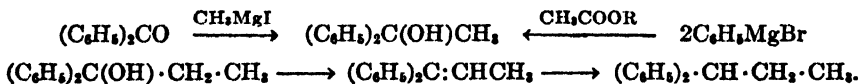
The group of *as*-diphenylethanes and the homologous *gem*-diphenyl paraffins will be dealt with first. The members of this series show marked resemblances to diphenylmethane and its derivatives, and at the same time they show genetic relationships with the dibenzyl group; *cf.* benzoic acid, diphenylacetaldehyde, stilbene, and tolane. Then follows the important group of dibenzyls, or *sym*-diphenylethanes, and then the  $\omega,\omega$ -diphenyl-propane, -butane-, -pentane-, and -hexane groups. The derivatives alkylated or phenylated in the benzene nuclei, or in the side-chains connecting them, are included with the parent hydrocarbons of the individual groups. The unsaturated hydrocarbons follow the saturated ones.

##### (a) *gem*-Diphenyl Paraffins and Their Derivatives

These may be produced by the following general methods: 1. By condensation of aldehydes, aldehydo-halides, glyoxylic acid, *etc.* with benzene hydrocarbons, phenols, or tertiary anilines, just as the diphenylmethanes are prepared from formaldehyde, methylene iodide, *etc.*:



2. Diphenylalkyl-carbinols are obtained by the condensation of benzophenone with alkyl magnesium iodides, or by the action of phenyl magnesium bromide on aliphatic esters, acid chlorides or anhydrides (*Grignard's reaction*). These carbinols readily split off water and form *gem*-diphenyl olefines, which can be reduced by sodium and alcohol to the *gem*-diphenyl paraffins:



All the substances of this group give benzophenone or its derivatives on oxidation:

*as*-Diphenylethane,  $(C_6H_5)_2CHCH_3$ , b.p.  $269^\circ$  (b.p.  $145^\circ$  (13 mm.)), is obtained by the action of benzene on paraldehyde in the presence of sulphuric acid, the reaction mixture being kept cold, and also by the action of benzene and aluminium chloride on ethylidene chloride,  $CH_3CHCl_2$ ,  $\alpha$ -bromo-ethylbenzene,  $C_6H_5 \cdot CHBrCH_3$ , styrene, or acetylene, and by reduction of *as*-diphenylethylene (see

\* The word *gem*- signifies that two equal groups are attached to one C atom; it is derived from *gemini*, twins (*Baeyer*, Ber. 31, 2068).

below) with sodium and alcohol or hydrogen and nickel at 230°. *as*-Diphenylethane is oxidised to benzophenone by chromic acid mixture, the methyl group being split off. For the action of aluminium chloride, see *Radziewanowski*, Ber. 27, 3238. When acted upon by nitric acid, *as*-diphenylethane is nitrated in the side-chain and not in the nucleus. The following substances are produced: diphenylethylene-glycol-mononitrite,  $(C_6H_5)_2C(OH) \cdot CH_2(ONO)$ , m.p. 100°, diphenylvinyl nitrite,  $(C_6H_5)_2C=CH \cdot (ONO)$ , m.p. 86°, and a dinitrite, m.p. 149°, which is possibly a derivative of diphenylethylene. The three compounds crystallise readily forming yellow crystals, and are converted into benzophenone by oxidation (*Anschütz*, Ann. 233, 330; *Konowalnw*, J. Russ. Phys.-Chem. Soc. 37, 542).

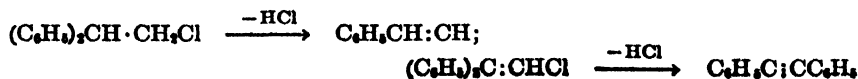
*as*-Phenolphenyethane,  $C_6H_5CH(CH_3)C_6H_4OH$ , m.p. 58°, is obtained from phenol and styrene when treated with sulphuric acid. The homologous phenols, naphthols, etc., react in a similar way with styrene (*Koenigs*, Ber. 24, 3891). The addition of styrene to the phenols takes place most readily in the *p*-position to the hydroxyl group. *as*-Diphenolethane,  $(C_6H_4OH)_2CHCH_3$ , m.p. 122°, is obtained by the action of aldehyde on phenol (*Claus*, Ber. 19, 3009). *as-p,p'*-Tetramethyl-diamino-diphenylethane,  $[(CH_3)_2NC_6H_4]_2CHCH_3$ , m.p. 69°, is broken down by nitrous acid into *p*-nitrodimethylaniline (*Trillat*, C.r. 128, 1404; 129, 1242).

*gem*-Diphenyl-propane, -butane, and -hexane, b.p. 142°, 150°, 164° (10 mm.), respectively, are obtained by the action of sodium and alcohol on the corresponding olefines (*Masson*, C.r. 135, 533) or by catalytic hydrogenation with nickel.

*gem*-Diphenyl-methyl-, -ethyl-, -propyl-, and -amyl-carbinols,  $(C_6H_5)_2C(OH)R$ , m.p. 81°, 95°, b.p. 185° (15 mm.), m.p. 47°, respectively, are obtained from benzophenone by the action of alkyl magnesium iodides, or from fatty acids and phenyl magnesium bromide, according to method 2 (see above). By distillation, or treatment with dehydrating agents, these carbinols yield: *gem*-diphenylethylene, -propylene-, -butylene-, and -hexylene, respectively, b.p. 270°, 280°, m.p. 52°, 292°, 314°, respectively. *as*-Diphenylethylene is also formed from  $\alpha$ -diphenyl- $\beta$ -chloroethane (see below), and from *as*-dibromoethylene by the action of benzene and aluminium chloride. It readily splits off formaldehyde by autoxidation. *gem*-Diphenylpropylene gives  $\alpha$ -diphenyl- $\beta$ -bromopropylene,  $(C_6H_5)_2C:CHCH_2Br$ , m.p. 49°, with bromine (*Klages*, Ber. 35, 2646; 37, 1447; *Hell*, Ber. 37, 230; *Masson*, C.r. 135, 533). *o*-Hydroxydiphenylethylene,  $HO[2]C_6H_4C(C_6H_5):CH_2$ , b.p. (13 mm.) 167°, see *Stoermer*, Ber. 36, 4002.

A series of halogen derivatives of monosubstituted diphenylethylenes, of the general formula, 
$$\begin{array}{c} C_6H_5 \\ \diagup \\ C_6H_4X \end{array} \begin{array}{c} H \\ \diagdown \\ C=C \\ \diagup \\ Hlg \end{array}$$
, exist in *cis-trans* isomeric forms. They can be converted from the *cis*- to the *trans*-form by ultra-violet light (*Stoermer*, Ann. 342, 1; Ber. 42, 4865).

*as*-Diphenyl-monochloroethane,  $(C_6H_5)_2CHCH_2Cl$ , is an oil. Diphenyl-dichloroethane,  $(C_6H_5)_2CHCHCl_2$ , m.p. 80°, diphenyl-trichloroethane,  $(C_6H_5)_2CHCCl_3$ , m.p. 64°, are formed by the action of benzene and sulphuric acid on mono-, di-, and trichloroacetaldehydes (chloral), respectively (*Fritsch*, Ann. 306, 72). When treated with alkali, these substances split off HCl giving *as*-diphenylethylene (see above). Diphenyl-monochloroethylene,  $(C_6H_5)_2C:CHCl$ , m.p. 42°, b.p. 298°, and diphenyl-dichloroethylene,  $(C_6H_5)_2C:CCl_2$ , m.p. 80°, b.p. 316°, are amongst the condensation products of chloral with benzene in the presence of aluminium chloride (*Biltz*, Ber. 26, 1955). When heated with sodium ethylate, diphenyl-dichloroethylene is converted into diphenylacetic acid (p. 555). If diphenyl-monochloroethane is heated by itself, the substance simultaneously loses HCl and undergoes a transformation, stilbene being formed. Stilbene is also formed when diphenyl-dichloroethane is treated with zinc dust and alcohol. Here again reduction is followed by transformation. When diphenyl-monochloroethylene is heated with a solution of sodium ethylate, diphenyl-vinyl-ethyl ether,  $(C_6H_5)_2C:CHOC_2H_5$ , is formed, together with tolane, the latter being produced by a transformation:

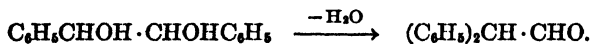


These reactions also extend to a series of substituted diphenylmono- and -trichloroethanes, and diphenyl-monochloroethylenes (*Fritzsche*, Ann. 279, 319; *Elbs*, J. pr. [2], 47, 44).

*as*-Diphenylethylene glycol,  $(C_6H_5)_2C(OH) \cdot CH_2OH$ , m.p.  $121^\circ$ , is obtained from ethyl glycolate or benzoyl carbinol (p. 403) by the action of phenyl magnesium bromide. In a similar manner diphenylpropylene glycol,  $(C_6H_5)_2C(OH) \cdot CHOH \cdot CH_2$ , m.p.  $96^\circ$ , is obtained from ethyl lactate, 1,1-diphenyl glycerol  $(C_6H_5)_2C(OH)CHOH \cdot CH_2OH$ , m.p.  $158^\circ$ , from ethyl glycerate, and diphenylethylene chlorhydrin,  $(C_6H_5)_2C(OH) \cdot CH_2Cl$ , m.p.  $66^\circ$ , from ethyl chloroacetate and phenyl magnesium bromide. When the last mentioned compound is warmed

with sodium ethylate, diphenylethylene oxide,  $(C_6H_5)_2\overline{C} : O \cdot CH_2$ , m.p.  $56^\circ$ , is formed (*Stoermer*, Ber. 39, 2288).

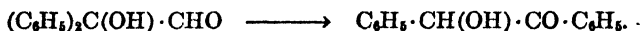
When diphenylethylene glycol is heated with 20% sulphuric acid, or diphenylethylene oxide is distilled *in vacuo*, diphenylacetaldehyde,  $(C_6H_5)_2CH \cdot CHO$ , b.p.  $166^\circ$  (9 mm.), is formed. Its oxime melts at  $120^\circ$ . The compound is also obtained by hydrolysis of diphenyl-vinyl-ethyl ether with glacial acetic and hydrochloric acids. In many ways it behaves like the hydroxymethylene compounds (p. 407, *etc.*). When oxidised it does not give an acid, but splits off the CHO group and gives benzophenone (*Auwers*, Ber. 24, 1780; *Claisen*, Ber. 25, 1781). Diphenylacetaldehyde is also formed from the hydrobenzoin by the action of dehydrating agents, the anhydrides being formed at the same time (p. 562):



This is due to an atomic rearrangement opposite to that mentioned above in connection with *as*-diphenylchloro-ethane and -ethylene, and is reminiscent of the pinacone rearrangement (see benzoic acid transformation).

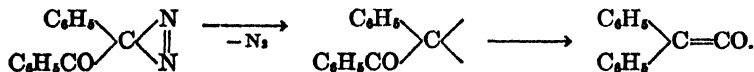
Methyl and ethyl-hydrobenzoin,  $C_6H_5CH(OH) \cdot C(Alk)OHC_6H_5$ , behave in the same way, giving  $\alpha$ , $\alpha$ -diphenylpropionaldehyde,  $(C_6H_5)_2C(CH_3) \cdot CHO$ , b.p.  $176^\circ$  (12 mm.), and,  $\alpha$ , $\alpha$ -diphenylbutyraldehyde,  $(C_6H_5)_2C(C_2H_5) \cdot CHO$ , b.p.  $314^\circ$  (*Tiffeneau*, C.r. 143, 1242).

Diphenylglycolic aldehyde, m.p.  $162^\circ$ , is obtained by heating bromodiphenylacetaldehyde with barium carbonate. With sulphuric acid in alcoholic solution it transposes to benzoin (*Danilow*, Ber. 60, 2390).



*as*-Diphenylacetone,  $(C_6H_5)_2CH \cdot COCH_3$ , m.p.  $45^\circ$  and  $61^\circ$  (dimorphous) (oxime, m.p.  $164^\circ$ ), is obtained by heating diphenylpropylene glycol (see above) with dilute hydrochloric acid (*Stoermer*, Ber. 39, 2302).

Diphenylketene,  $(C_6H_5)_2C : CO$ , b.p.  $146^\circ$  (12 mm.), a reddish-yellow liquid, which crystallises in the refrigerator to straw-yellow crystals, was the first member of this interesting class of compounds, the ketenes, to be discovered (*Staudinger*, 1905) (see Vol. I, p. 269). It is obtained by the action of zinc on diphenylchloroacetyl chloride (p. 556) or by removal of HCl from diphenylacetyl chloride by means of tertiary bases (*Staudinger*, Ann. 356, 51). Its very ready formation from azibenzil (p. 565) with splitting off of  $N_2$  and wandering of a phenyl group is particularly interesting (*Schroeter*, Ber. 42, 2346):



This is a reaction which is analogous to the formation of stilbene from diphenyl-monochloroethylene (p. 553) and of tetraphenyl-ethylene from benzpinacoline-alcohol (p. 575).

Diphenylketene is more stable than the aliphatic ketenes, and shows no tendency towards polymerisation. It is, however, extremely reactive. 1. With water it forms diphenylacetic acid or its anhydride. 2. With alcohols it forms diphenylacetic esters. 3. With hydrochloric acid it gives diphenylacetyl chloride. 4. With ammonia, phenylhydrazine, primary and secondary bases it gives the corresponding diphenylacetic acid derivative. 5. With organic acids it forms mixed acid anhydrides. 6. With sodio-malonic ester it gives diphenyl-acetyl-



dinitrophenyl radical into dinitro-phenylacetic ester (p. 320). The ester forms salts with potassium and sodium which possess a metallic lustre, and dissolve in alcohol and water giving dark blue solutions; cf. the similar behaviour of tetra-nitro-diphenylmethane and trinitro-triphenylmethane,  $[(\text{NO}_2)_2\text{C}_6\text{H}_4]_2\text{CH}_2$  and  $(\text{NO}_2)_3\text{C}_6\text{H}_4\text{CH}_3$ , respectively (pp. 511, 526), and trinitro-phenylmalonic ester (p. 434) (*Richter*, Ber. 21, 2476).

*p,p'*-Diamino-diphenylacetic acid,  $[\text{NH}_2\text{C}_6\text{H}_4]_2\text{CHCOOH}$ , m.p.  $234^\circ$ , is obtained by the transposition of dianilidoacetic acid,  $(\text{C}_6\text{H}_5\text{NH})_2\text{CHCOOH}$ , (p. 91) on heating with aniline and aniline hydrochloride (*Ostrowskiesky*, Ber. 41, 3019, 3031).

*p*-Hydroxy-diphenylacetic acid, m.p.  $173^\circ$ , is obtained from mandelic acid or its nitrile by the action of phenol and 73 per cent sulphuric acid. *o*-Hydroxy-

diphenylacetic lactone,  $\text{C}_6\text{H}_5\text{CH} \begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$ , m.p.  $114^\circ$ , is a by-product. The

latter gives a bromo-derivative which is easily converted into *o*-hydroxy-diphenylglycocol,  $\text{HOC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_5)(\text{NH}_2)\text{COOH}$  (*Bistrzycki*, Ber. 31, 2812).

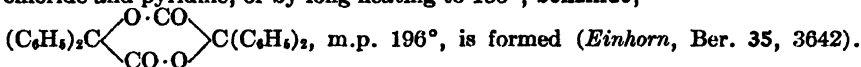
Tetrahydroxy-diphenylacetic acid,  $[\text{C}_6\text{H}_4(\text{OH})_2]_2\text{CHCOOH}$ , is obtained by the condensation of chloral with resorcinol in the presence of potassium bisulphate. It is yellow in colour, but dissolves in cold alkalis with a red colour, and gives a triacetyl derivative, m.p.  $152^\circ$  (*Hewitt*, J. 69, 1265; 71, 1084).

Benzilic acid, diphenylglycolic acid,  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{COOH}$ , m.p.  $150^\circ$ , is obtained from diphenylacetic acid by the action of bromine and water, and from benzil by warming with alcoholic potash, or fusing with potash, an intramolecular transformation taking place (preparation, see *Staudinger*, Ann. 356, 71; *Liebig*, Ber. 41, 1644). It is also prepared by boiling benzoin with aqueous potash, and bubbling air through to act as an oxidising agent (*Montagne*, Rec. 21, 6):



When heated above its melting point, benzilic acid takes on a blood-red colour, and its solution in concentrated sulphuric acid is also this colour. By thermal decomposition in the presence of traces of alkali it gives tetraphenyl-cyclobutane-dione-1,2 (Vol. IV). By the action of cold concentrated sulphuric acid on benzilic acid, derivatives of diphenylene-phenylethane are formed (*q.v.*, *Klinger*, Ber. 29, 734).

Benzilic acid gives diphenyl-chloroacetic acid,  $(\text{C}_6\text{H}_5)_2\text{CClCOOH}$ , m.p.  $119^\circ$  (decomp.), and diphenyl-chloroacetyl chloride, m.p.  $50^\circ$  (*Staudinger*, Ann. 356, 72), with chlorides of phosphorus. With phosphorus pentoxide, or carbonyl chloride and pyridine, or by long heating to  $155^\circ$ , benzilide,



With hydriodic acid and phosphorus it is reduced to diphenylacetic acid, and on distillation of its barium salt it gives diphenylcarbinol (p. 512). When oxidised it gives benzophenone.

*p*-Tolilic acid,  $(\text{CH}_3\text{C}_6\text{H}_4)_2\text{C}(\text{OH})\text{COOH}$ , anisilic acid,  $(\text{CH}_3\text{OC}_6\text{H}_4)_2\text{C}(\text{OH})\text{COOH}$ , cumililic acid,  $(\text{C}_6\text{H}_7\text{C}_6\text{H}_4)_2\text{C}(\text{OH})\text{COOH}$ , and hexamethoxybenzilic acid  $[(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3]_2\text{C}(\text{OH})\text{COOH}$ , are obtained by similar methods to benzilic acid, from the corresponding substituted benzils (p. 568).

$\beta,\beta$ -Diphenylpropionic acid,  $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COOH}$ , m.p.  $149^\circ$ , is homologous with diphenylacetic acid. It is obtained by the action of phenyl magnesium bromide on ethyl cinnamate (*Kohler*, Am. 33, 21), or by the action of benzene on cinnamic acid in the presence of sulphuric acid, in the same way as phenol-phenyl-ethane is obtained from styrene and phenol (p. 553). By the further action of sulphuric acid it condenses to 3-phenylhydrindone (p. 592).  $\alpha$ -Bromo- $\beta,\beta$ -diphenylpropionic acid, m.p. about  $164^\circ$ , and its potassium salt even more readily, breaks down on boiling the aqueous solution into carbon dioxide, hydrobromic acid, and stilbene (p. 559), a reaction which corresponds to the formation of this hydrocarbon from diphenyl-monochloroethylene (p. 553) (*Kohler*, Am. 34, 132). Phenyltolyl- and phenylxylyl-propionic acids, etc., are obtained similarly to diphenylpropionic acid (*Karsten*, Ber. 26, 1579). When oxidised these acids

give benzophenone, phenyltolyl ketone, phenylxylyl ketone, etc.  $\gamma,\gamma$ -Diphenylbutyric acid,  $(C_6H_5)_2CHCH_2CH_2\cdot COOH$ , m.p.  $107^\circ$ , is obtained from  $\gamma$ -phenylbutyrolactone (p. 418), or "phenylisocrotonic acid" (p. 469) by the action of benzene and aluminium chloride (*Eijkman*, *Chem. Weekbl.* 4, 727).

$\alpha,\alpha$ -Diphenylpropionic acid,  $(C_6H_5)_2C(CH_3)COOH$ , m.p.  $173^\circ$ , and its homologues are obtained by the condensation of phenylpyruvic acid (p. 428) with benzene and its homologues with concentrated sulphuric acid (*Böttlinger*, *Ber.* 14, 1595). On heating with concentrated sulphuric acid they split off carbon monoxide and form diphenyl-carbinols, which, in their turn, readily break down into water and *as*-diaryl-ethylenes (*Bistrzycki*, *Ber.* 38, 839).

$\beta$ -Diphenylpyruvic acid,  $(C_6H_5)_2CH\cdot CO\cdot COOH$ , is obtained by the condensation of benzophenone and ethyl chloroacetate (*Troell*, *Ber.* 61, 2497).

$\beta$ -Phenylcinnamic acid,  $(C_6H_5)_2C:CH\cdot COOH$ , m.p.  $162^\circ$ , is obtained in a similar way to the  $\beta$ -alkylcinnamic acids from the condensation product of benzophenone with ethyl bromoacetate and zinc (*Rupe*, *Ber.* 40, 4537; *Stoermer*, *Ber.* 41, 324). It is also obtained by the action of alcoholic potash on  $\alpha$ -bromo- $\beta$ -diphenylpropionic acid (*Kohler*, *Am.* 33, 21).

$\gamma$ -Diphenylitaconic acid,  $(C_6H_5)_2C:C(COOH)\cdot CH_2COOH$ , m.p.  $169^\circ$  (decomp.). The ester of this acid is obtained by condensation of benzophenone and ethyl succinate in the presence of sodium ethylate. When heated under reduced pressure, the acid gives an anhydride, m.p.  $147$ – $150^\circ$ , and when this is dissolved in caustic soda and acidified, diphenylcitraconic acid,  $(C_6H_5)_2CHC(COOH):CHCOOH$ , m.p.  $110$ – $115^\circ$  (decomp.), is formed. With concentrated sulphuric acid, diphenylitaconic acid condenses to phenylindone-acetic acid; with bromine

it gives  $\gamma$ -diphenyl-bromo-paraconic acid,  $(C_6H_5)_2C\cdot CBr(COOH)\cdot CH_2\cdot COO$ , which, when warmed with water is converted into  $\gamma$ -diphenylitaconic acid, m.p.  $139^\circ$ , and further, with loss of carbon dioxide into  $\gamma$ -diphenylcrotonic lactone,

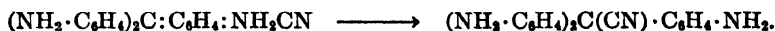
$(C_6H_5)_2C\cdot CH:CH\cdot COO$ , m.p.  $131^\circ$  (*Stobbe*, *Ann.* 308, 89).  $\gamma$ -Diphenyl- $\alpha,\beta$ -dichlorocrotonic acid,  $(C_6H_5)_2CH\cdot CCl:CClCOOH$ , m.p.  $152^\circ$ , is formed from chloromucconyl chloride, benzene, and aluminium chloride (*Dunlap*, *Am.* 19, 641).  $\beta,\beta$ -Diphenylacetyl-acrylic ester,  $(C_6H_5)_2C:C(COCH_3)COOC_2H_5$ , m.p.  $76^\circ$ , obtained from diphenyl-dichloromethane and copper acetoacetic ester gives diphenylbutenone,  $(C_6H_5)_2C:CHCOCH_3$ , m.p.  $33^\circ$ , b.p.  $190^\circ$  (13 mm.) by ketonic fission (*Klages*, *Ber.* 32, 1433).

1,1,1-Triphenylethane,  $(C_6H_5)_3C\cdot CH_3$ , m.p.  $95^\circ$ , -propane, m.p.  $51^\circ$ , -butane, m.p.  $79^\circ$ , and homologues are obtained by the action of alkyl magnesium halides on triphenyl-chloromethane (*Gomberg*, *Ber.* 39, 2957).

Triphenylacetaldehyde,  $(C_6H_5)_3C\cdot CHO$ , m.p.  $106^\circ$ , obtained from  $\alpha,\alpha,\beta$ -triphenylethylene glycol by boiling with sulphuric acid, is transformed by acids into diphenyl-acetophenone,  $(C_6H_5)_2CHCOC_6H_5$ , m.p.  $136^\circ$  (*Danilow*, *J. Russ. Phys.-Chem. Soc.* 51, 97). Triphenylmethyl-ethyl-ketone,  $(C_6H_5)_3C\cdot COC_2H_5$ , m.p.  $104^\circ$ , is obtained by the action of triphenylacetyl chloride on ethyl magnesium iodide (*Schmidlin*, *Ber.* 43, 1137).

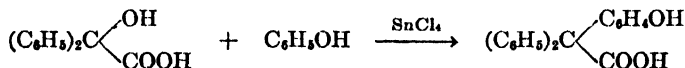
Triphenylacetic acid,  $(C_6H_5)_3C\cdot COOH$ , m.p.  $265^\circ$  (decomp.), breaks down on heating into carbon dioxide and triphenylmethane. It is a very weak acid, like its substitution products. It is isomeric with the triphenylmethane carboxylic acids described earlier (p. 543). It is obtained by the action of carbon dioxide on phenyl magnesium chloride (*Schmidlin*, *Ber.* 39, 634). It can also be obtained from trichloroacetic acid or diphenylchloroacetic acid by the action of benzene and aluminium chloride (*Bistrzycki*, *Ber.* 36, 145), by passing carbon dioxide through potassium triphenylmethyl (p. 525), at  $200^\circ$ , or by the action of carbon dioxide on triphenylmethyl-magnesium chloride. When warmed with concentrated sulphuric acid, it breaks down into carbon monoxide and triphenyl-carbinol (p. 528). In a similar way, its chloride, m.p.  $128^\circ$ , gives triphenyl-chloromethane. It is very difficult to esterify. Its esters decompose on heating, losing carbon dioxide. Methyl ester, m.p.  $186^\circ$ , phenyl ester, m.p.  $123^\circ$ , triphenylmethyl ester, m.p.  $185^\circ$  (*Anschütz*, *Ann.* 359, 196). Amide, m.p.  $246^\circ$ , anhydride, m.p.  $163^\circ$  (*Schmidlin*, *Ber.* 41, 438). Its nitrile, m.p.  $127^\circ$ , is obtained from triphenyl-chloro- or -bromomethane by the action of mercuric cyanide (*Fischer*, *Ann.* 194, 260; *Meyer*, *Ber.* 28, 2782), or by de-amination of hydrocyano-*para*rosaniline (*Fischer*, *Ber.* 26, 2225). *p,p',p''*-Triamino-triphenylacetoneitrile, hydrocyano-

pararosaniline, is obtained from the pararosaniline salts by warming with alcohol and potassium cyanide. In a similar way, hydrocyanorosaniline is obtained from rosaniline salts. According to *Hantzsch*, a quinoid ammonium cyanide is first formed, which transposes to the nitrile in the solution (Ber. 33, 287):



The hydrochlorides of these hydrocyano-compounds decompose on heating into HCl, HCN, and rosaniline hydrochlorides.

Substituted triphenylacetic acids, especially phenol derivatives, are readily obtained by the condensation of benzoic acid with phenols by means of stannic chloride (*Bistrzycki*, Ber. 34, 3080; 37, 664; 40, 4060):

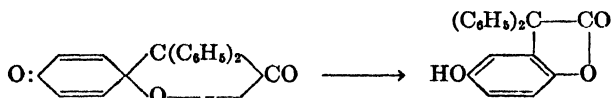


Diphenyl-*p*-tolylacetic acid,  $\text{CH}_3[4]\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{CCOOH}$ , m.p. 205°; *p*-tri-tolylacetic acid,  $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{C} \cdot \text{COOH}$ , m.p. 227°; *p*-hydroxytriphenylacetic acid,  $\text{HO}[4]\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{CCOOH}$ , m.p. 212° (decomp.); *m*- and *p*-cresyl-

diphenylacetic lactone,  $\text{O}[2]\text{C}_6\text{H}_3(\text{CH}_3)[1]\text{C}(\text{C}_6\text{H}_5)_2\text{CO}$ , m.p. 126° and 130°, respectively. *o*- and *m*-Xylenyl-diphenylacetic lactone, m.p. 178° and 170°, respectively. Thymyl- and carvacryl-diphenylacetic acid,  $\text{HO}[4]\text{C}_6\text{H}_3(\text{CH}_3)-(\text{C}_2\text{H}_7)[1]\text{C}(\text{C}_6\text{H}_5)_2\text{COOH}$ , etc.

$\beta$ -Triphenyl-lactic acid,  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$ , is obtained from benzophenone and phenylacetic acid under the influence of light (*Paterno*, Gazz. 40, II, 321). It readily splits off water, becoming 1,2-diphenylindone (p. 596) (*de Fazi*, Atti. R. Accad. Lincei [5] 24, I, 439).

Diphenylmethyl-quinolcarboxylic lactone (formula, see below), colourless crystals, m.p. 143°, is obtained by condensation of diphenylketene with excess of quinone (cf. p. 554). On heating it breaks down into carbon dioxide and diphenylquinomethane (p. 539). Like all quinone derivatives it shows the characteristic transformation into benzene derivatives with migration of the alkyl group. Thus, the above  $\beta$ -lactone when illuminated in the solid state or in boiling benzene solution passes into the isomeric 2,5-dihydroxy-triphenylacetic lactone, m.p. 196°:



which can also be obtained synthetically from hydroquinone and benzoic acid in the presence of stannic chloride (*Staudinger*, Ann. 380, 248).

### (b) sym-Diphenylethane Group

Dibenzyl, *sym*-diphenylethane,  $\text{C}_6\text{H}_5\text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$ , m.p. 52°, b.p. 284°, is obtained: 1. by the action of sodium, magnesium, or copper on benzyl chloride (*Michailenko*, J. Russ. Phys. Chem. Soc. 53, 347); 2. by the action of benzene on ethylene chloride, or chloroethylbenzene, in the presence of aluminium chloride (*Anschütz*, Ann. 235, 155); 3. from acetylene, benzene, and concentrated sulphuric acid in the presence of mercury salts (*Reichert*, Am. 45, 3090); 4. from its oxygen-containing derivatives, benzoin, benzil, etc., and from the unsaturated hydrocarbons stilbene and tolane, by reduction with sodium and alcohol, hydriodic acid, or hydrogen and nickel at 220° (*Sabatier*, C.r. 145, 1126); 5. by oxidation of toluene with potassium persulphate (*Moritz*, Ber. 32, 2531).

When heated to 500°, dibenzyl forms stilbene and toluene (see also phenanthrene). By oxidation with chromic acid or permanganate it is converted into benzoic acid. Two dinitro-dibenzyls are obtained by nitration of dibenzyl: *p,p'*-dinitrodibenzyl, m.p. 181°, which can also be obtained from *p*-nitrobenzyl chloride and stannous chloride (Roser, Ann. 238, 273; Heumann, Ber. 20, 909), and by the action of cold, methyl alcoholic potash on *p*-nitrotoluene (Green, Proc. 23, 289; J. 91, 2076). *o,o'*-Dinitrodibenzyl, m.p. 122° (Duval, Bull. [4], 7, 485, 527, 677, 727).

*p,p'*-Diaminodibenzyl can be used for the preparation of tetrazo-dyes, in the same way as diaminostilbene (Ger. Pat. 101,861).

*o,o'*-Diaminodibenzyl, m.p. 68°, obtained by the reduction of *o,o'*-diaminostilbene; when its hydrochloride is heated it gives iminodibenzyl,

$\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$ , m.p. 110°, which contains a seven-membered ring (Thiele, Ann. 305, 96).

**Homologues of dibenzyl:** *o,o'*-, *m,m'*- and *p,p'*-dimethyldibenzyl, m.p. 66°, 82° and b.p. 296°, are obtained by the oxidation of *o*-, *m*-, and *p*-xylene, respectively, with potassium persulphate (Moritz, Ber. 32, 2531).

**Dimesitylethane**, b.p. 344–348° (Reichert, Am. 45, 3090).

**$\alpha,\beta$ -Diphenylpropane**,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5$ , b.p. 167° (28 mm.), is obtained by the reduction of  $\alpha$ -methylstilbene (p. 560).  **$\alpha,\beta$ -Diphenylisobutane**,  $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_5$ , is obtained from isobutylene bromide, benzene, and aluminium chloride (Bodroux, C.r. 132, 1333).

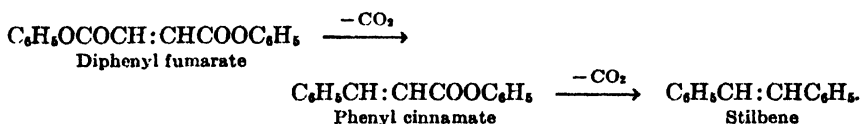
**$\alpha,\beta$ -Phenyltolylpropane** and  **$\alpha,\beta$ -phenylxyllylpropane** are obtained from styrene by the action of xylene or trimethylbenzene and concentrated sulphuric acid. One methyl group of the benzene homologue adds on across the double bond of the styrene (Kraemer, Ber. 23, 3269). **Diphenyl-dimethylethane**,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ , m.p. 123°, is obtained by the action of sodium or zinc dust on  $\alpha$ -halogeno-ethylbenzene, or by the oxidation of ethylbenzene with potassium persulphate (Schramm, Ber. 26, 1710; Moritz, Ber. 32, 434).

**Diphenyl-diethylethane**,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_2\text{H}_5)\text{CH}(\text{C}_2\text{H}_5)\text{C}_6\text{H}_5$ , is obtained by the action of sodium on the bromide of ethyl-phenyl carbinol. It exists in two stereoisomeric forms, one m.p. 90°, the other a liquid at ordinary temperatures. They can be converted into one another (Lepin, J. Russ. Phys.-Chem. Soc. 47, 149).

**Stilbene**, *sym*-diphenyl-ethylene, or *toluylene*,  $\text{C}_6\text{H}_5\text{CH}:\text{CHC}_6\text{H}_5$ , m.p. 124°, b.p. 167° (12 mm.), crystallises in large glistening ( $\sigma\tau\lambda\beta\epsilon\upsilon\nu$ , lustrous) monoclinic leaflets or prisms. It is produced by a great variety of reactions, and is one of the longest-known of aromatic substances (Laurent, 1844). It is formed: 1. By heating benzyl sulphide or benzyl disulphide (Fromm, Ber. 36, 538). 2. By heating polymeric thiobenzaldehyde (p. 271) to 300°, or by distillation of trithiobenzaldehyde with copper. 3. By the action of sodium on benzaldehyde or benzalchloride. 4. From benzaldehyde and phenylacetic acid, when stilbene is formed instead of the phenyl-cinnamic acid expected (von Walther, J. pr. [2], 61, 169). 5. Stilbene and its homologues are formed by the *Grignard reaction*, using benzyl magnesium chloride and benzaldehydes or aromatic ketones. The benzyl-aryl carbinols first formed split off water. 6. By heating *aci*-nitrobenzyl cyanide,  $\text{C}_6\text{H}_5\text{C}(\text{NOOH})\text{CN}$ , with caustic soda to high temperatures. Phenyl-*aci*-nitromethane is first formed, but splits off sodium nitrite giving stilbene (Wislicenus, Ber. 38, 502). 7. By heating benzalazine,  $\text{C}_6\text{H}_5\text{CH}:\text{N}:\text{N}:\text{CHC}_6\text{H}_5$  (p. 260), or phenyldiazomethane,  $\text{C}_6\text{H}_5\text{CHN}_2$  (p. 272), when nitrogen is split off. 8. By heating chlorinated *as*-diphenylethane derivatives, such as  $(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{CH}_2\text{Cl}$ ,  $\text{C}_6\text{H}_5\text{CH}\cdot\text{CCl}_3$  (p. 553), or treating them with zinc dust, when transposition occurs (Kipp, Ber. 7, 1409; Elbs, J. pr. [2],



47, 44; *Feuerstein*, Ber. 34, 415). 9. By the action of copper potassium hydrogen sulphide, or potassium cyanide on stilbene dihalides (*Anschütz*, Ber. 11, 1219). 10. A peculiar reaction is the formation of stilbene by the distillation of phenyl fumarate or phenyl cinnamate (*Anschütz*, Ber. 18, 1945):



See also the decomposition of chlorobenzyl-desoxybenzoin (p. 578) into benzoyl chloride and stilbene.

Since it is an unsaturated compound, stilbene can exist in a second, stereoisomeric form. This *isostilbene* is a liquid, b.p. 143° (12 mm.), and has a striking flower-like smell. It is obtained by reduction of tolane (p. 561) or isobromostilbene (p. 569) with zinc dust and alcohol (*Straus*, Ann. 342, 208). It can also be obtained from ordinary stilbene by irradiation in benzene solution with ultra-violet light (*Stoermer*, Ber. 42, 4871), when the polymer, *distilbene*, C<sub>22</sub>H<sub>24</sub>, m.p. 163°, is also formed (*Ciamician*, Ber. 35, 4129). It is converted into the stable, solid form of stilbene by the addition of traces of iodine or bromine, distillation under ordinary pressure, or by the action of the vapour of fuming nitric acid. *Isostilbene* has the *cis*-configuration: HC·C<sub>6</sub>H<sub>5</sub>. In agreement with this for-

mula lies the fact that it can be obtained from *cis*-α-phenyl-cinnamic acid by loss of carbon dioxide. The *trans*-allo-α-phenyl-cinnamic acid gives stilbene, to which is ascribed the *trans*-configuration, HC·C<sub>6</sub>H<sub>5</sub>, under the same treatment

(*Stoermer*, Ann. 409, 13).

When heated with hydriodic acid, stilbene is converted into dibenzyl. Halogens and halogen acids add on to stilbene, forming stilbene dihalides and halogen derivatives of hydrobenzoin, respectively. Chromic acid oxidises it to benzaldehyde and benzoic acid. By heating for a long time with sulphur to 250°, it is converted into *thionessal*, or tetraphenyl-thiophene. On heating to redness it gives phenanthrene. Stilbene combines with N<sub>2</sub>O<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> to give C<sub>14</sub>H<sub>12</sub>(N<sub>2</sub>O<sub>2</sub>) and C<sub>14</sub>H<sub>12</sub>(N<sub>2</sub>O<sub>4</sub>). By boiling with glacial acetic the former is partially decomposed into the latter, which is regarded as diphenyl-dinitroethane, C<sub>6</sub>H<sub>5</sub>·CH(NO<sub>2</sub>)·CH(NO<sub>2</sub>)·C<sub>6</sub>H<sub>5</sub>, α-modification, m.p. 236° (decomp.), β-modification, m.p. 150–152° (cf. p. 564 and *Schmidt*, Ber. 34, 3536). When treated with sodium methylate this compound splits off a molecule of nitrous acid, giving α-nitrostilbene, C<sub>6</sub>H<sub>5</sub>CH:C(NO<sub>2</sub>)C<sub>6</sub>H<sub>5</sub>, m.p. 75°, which can also be obtained by condensation of phenyl-nitromethane and benzaldehyde with aliphatic bases (*Knoevenagel*, Ber. 37, 4509). When α-nitrostilbene is heated with methyl alcoholic potash, and then with hydrochloric acid, it is converted, via a number of intermediate products, into the isomeric benzil monoxime, C<sub>6</sub>H<sub>5</sub>COC(NO<sub>2</sub>)C<sub>6</sub>H<sub>5</sub> (*Meissenheimer*, Ann. 355, 269).

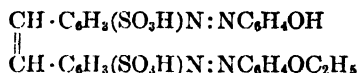
α-Methylstilbene, C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>):CHC<sub>6</sub>H<sub>5</sub>, f.p. 83°, b.p. 183° (26 mm.), and α-ethylstilbene, m.p. 57°, b.p. 296°, are obtained from desoxybenzoin and methyl- or ethyl-magnesium iodide, respectively. They can also be obtained from acetophenone by the action of benzyl magnesium chloride (*Hell*, Ber. 37, 457; *Klages*, Ber. 37, 1450; *Tiffeneau*, C.r. 139, 481).

*Stilbenes substituted* in the benzene nucleus are obtained from substituted benzyl- or benzal chlorides, and by condensation of substituted benzaldehydes with phenylacetic acid. Thus, *o,o'*-dichlorostilbene, (ClC<sub>6</sub>H<sub>4</sub>·CH)<sub>2</sub>, m.p. 97°, is obtained from *o*-chlorobenzal chloride by the action of copper, and dichlorodinitrostilbene, m.p. 294°, is obtained by the action of alcoholic potash on chloronitrobenzyl chloride (*Witt*, Ber. 25, 79; *Green*, J. 85, 1736).

Like the two stereoisomeric stilbenes, many of the substituted stilbenes can be converted into *iso*-forms by irradiation with ultra-violet light (*Stoermer*, Ann. 409,

29; Ber. 55, 1232). Some members of this series show chromoisomerism. Thus 4-nitro-4'-hydroxystilbene and its methyl ether can exist in a golden yellow and a greenish yellow form. 2,4-Dinitro-4'-hydroxystilbene, m.p. 158°, exists in a yellow and a red form (Stoermer, Ber. 55, 1232; Cullinane, J. 123, 2053).

*o,p*-Dinitrostilbene,  $(\text{NO}_2)_2[2,4]\text{C}_6\text{H}_3\text{CH}:\text{CHC}_6\text{H}_5$ , m.p. 140°, obtained from benzaldehyde and *o,p*-dinitrotoluene with piperidine as condensing agent, gives *o*-nitro-*p*-aminostilbene, m.p. 111°, when partially reduced with ammonium sulphide. With stannous chloride it is reduced to *o*-amino-*p*-nitrostilbene, m.p. 143°, and then to *o,p*-diaminostilbene, m.p. 120°. By the action of alcoholic potash on *o*- and *p*-nitrobenzyl chloride, two isomeric *o,o'*-dinitrostilbenes, m.p. 126° and 196°, and *p,p'*-dinitrostilbenes, m.p. 210–216° and 286°, are formed (Bischoff, Ber. 21, 2072; Walden, Ber. 23, 1959; Fischer, Ber. 26, 2232). On reduction, these compounds give the corresponding diaminostilbenes. *p,p'*-Dinitrostilbene-disulphonic acid is produced by the oxidation of *p*-nitrotoluene-sulphonic acid with alkali hypochlorite. *o,o'*-Dinitro-dibenzyl-disulphonic acid is first formed. Further oxidation gives rise to *p*-nitro-benzaldehyde-*o*-sulphonic acid (Herz, Proc. 1897, 125; Ger. Pat. 106,961). *o,o'*-Diaminostilbene, *cis*-form, m.p. 123°, *trans*-form, m.p. 168°, gives a good yield of indol when equivalent quantities of the hydrochloride and the base are heated. Aniline is split off (Thiele, Ber. 28, 1411); cf. on the other hand, *o,o'*-diaminodibenzyl, p. 559. The disulphonic acid of *p,p'*-diaminostilbene, m.p. 227°, gives a bis-diazonium compound, brilliant yellow, when diazotised and combined with phenol. The mono-ethyl derivative of the latter,



is the substantive cotton dye, *chrysophenin* (Meyer, Ber. 27, 3357). For further dyestuffs derived from stilbene, see Ger. Pat. 46,971 (see also benzidine dyes, p. 499). For the electrolytic reduction of nitrostilbene to cyclic azo- and azo-stilbenes, see Elbs, Z. Elektrochem. 9, 416.

*o*-Hydroxystilbene, m.p. 147° (Kostanecki, Ber. 42, 825). *p*-Hydroxystilbene, m.p. 189°, see Zincke, Ann. 349, 107.

*o,o'*-Dihydroxystilbene, m.p. 92°, is obtained, together with other products, by boiling salicylaldehyde with zinc dust and glacial acetic acid (Tiemann, Ber. 24, 3175).

*p,p'*-Dihydroxystilbene, m.p. 281°, is obtained from the condensation product of phenol and chloral, *as*-diphenol-trichloroethane,  $(\text{HO}[4]\text{C}_6\text{H}_4)_2\text{CHCCl}_3$ , by treatment with zinc dust or iron powder. At low temperatures bromine adds on to it forming *p,p'*-dihydroxystilbene dibromide, which has the nature of a *pseudo*-phenol, and that of an aliphatic bromide. When treated with sodium acetate it splits off two molecules of hydrogen bromide forming stilbene-quinone,  $\text{O}:\text{C}_6\text{H}_4:\text{CH}:\text{CH}:\text{C}_6\text{H}_4:\text{O}$ , bright red needles. This compound can also be obtained directly from *p,p'*-dihydroxystilbene by oxidation with lead dioxide or ferric chloride. Chemically it resembles the simple methylene-quinones (Zincke, Ann. 335, 157; Willstätter, Ber. 39, 3490). At higher temperatures chlorine and bromine simultaneously substitute and add on to *p,p'*-dihydroxystilbene, forming tetrachloro- and tetrabromo-*p,p'*-dihydroxystilbene dichloride, or dibromide, respectively. With alkali, these compounds give tetrabromo- and tetrachloro-stilbene-quinones,  $\text{O}:(\text{C}_6\text{Cl}_2\text{H}_2):\text{CH}:\text{CH}:(\text{C}_6\text{Cl}_2\text{H}_2):\text{O}$ , respectively. They are difficultly soluble substances, which resemble amorphous phosphorus in appearance (Zincke, Ann. 325, 19).

3,5,3',5'-Tetramethyl-4,4'-stilbene-quinone,  $\text{O}:\text{C}_6\text{H}_2(\text{CH}_3)_2:\text{CH}:\text{CH}:(\text{CH}_3)_2:\text{C}_6\text{H}_2:\text{O}$ , is obtained by oxidation of mesitol with silver oxide (Goldschmidt, Ber. 56, 1963).

3,4-Methylene-dioxystilbene,  $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}:\text{CHC}_6\text{H}_5$ , m.p. 96°, is obtained from piperonal (p. 349) and benzyl magnesium chloride (Hell, Ber. 37, 1431).

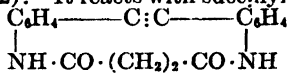
Tolane, diphenylacetylene,  $\text{C}_6\text{H}_5\text{C}:\text{CC}_6\text{H}_5$ , m.p. 62.5°, is obtained by the action of mercuric oxide on benzil-dihydrazone, and splitting off nitrogen from benzil-diazide (Schlenk, Ann. 463, 76). It is also

obtained by boiling stilbene dibromide with alcoholic potash, and by the action of sodium ethylate on *as*-diphenylchloroethylene,  $(C_6H_5)_2C:CHCl$ , when diphenylvinylethyl ether (p. 553) is a by-product.

The substituted tolans are more smoothly obtained by the last-mentioned method: 4,4'-dimethyltolane, m.p.  $136^\circ$ , 4,4'-dimethoxytolane, m.p.  $145^\circ$ , obtained from ditolyl- and dianisyl-chloroethylene, respectively (*Buttenberg*, Ann. 279, 324). *o,o'*-Dichlorotolane, m.p.  $89^\circ$ , from *o,o'*-dichlorostilbene dichloride. Tetrachloro-*p*-dihydroxytolane, m.p.  $226^\circ$ , see *Zincke*, Ann. 338, 236.

Tolane adds on two and four halogen atoms, and gives tolane di- and tetrachloride (p. 568). The tolane chlorides can also be obtained by the action of calcium carbide and chlorine on benzene (*Davidson*, Am. 40, 397).  $\alpha$ -Tolane dichloride,  $C_6H_5-C \cdot Cl = C \cdot Cl-C_6H_5$ , m.p.  $143^\circ$ . They lose the elements of water when treated with glacial acetic acid and sulphuric acid, forming desoxybenzoins. By the action of oxides of nitrogen on tolane,  $\alpha$ - and  $\beta$ -diphenyldinitroethylene,  $C_6H_5C(NO_2):C(NO_2)C_6H_5$ , m.p.  $186-187^\circ$  and  $105-107^\circ$ , respectively, are formed (*Schmidt*, Ber. 34, 619). *p,p'*-Dinitrotolane, yellow leaflets, m.p.  $207-210^\circ$ , is obtained by the action of caustic potash on *p,p'*-dinitrostilbene dibromide. On reduction it gives *p,p'*-diaminotolane, m.p.  $236^\circ$ , which is converted into diamino-desoxybenzoin, m.p.  $145^\circ$ , on warming with dilute acids (*Reinhardt*, Ber. 46, 3598).

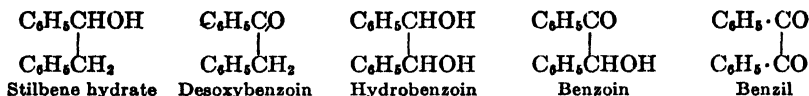
*o,o'*-Dinitrotolane, m.p.  $192-193^\circ$ , is obtained by the action of alcoholic potash on nitrobenzal chloride, or from *o,o'*-dinitrostilbene dichloride. *o,o'*-Diaminotolane, m.p.  $154^\circ$ , is obtained by reduction of the nitro-compound (*Kliegl*, Ber. 44, 1209; *Pfeiffer*, Ber. 45, 1828; *Ruggli*, Ann. 392, 92). It reacts with succinyl chloride, forming cyclosuccinyl-diaminotolane:



m.p.  $237-238^\circ$ , a compound with a 12-membered ring and a triple bond. By reaction between the diamines and the corresponding chlorides, rings with up to 17 members can be prepared (*Ruggli*, Ann. 399, 174).

*o,p*-Dinitrotolane, a yellow substance, m.p.  $112^\circ$ .

#### 1. ALCOHOL AND KETONE DERIVATIVES OF DIBENZYL:



**Stilbene hydrate**, *benzyl-phenyl carbinol*,  $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot C_6H_5$ , m.p.  $67^\circ$ , is obtained by the reduction of desoxybenzoin with sodium amalgam, and by the action of benzaldehyde on benzyl magnesium chloride. **Benzyl-phenyl-methyl-carbinol**,  $C_6H_5C(OH)(CH_3) \cdot CH_2C_6H_5$ , m.p.  $51^\circ$ , b.p.  $175^\circ$  (15 mm.), is obtained in a similar way by the action of acetophenone on benzyl magnesium chloride, or by the action of methyl magnesium iodide on desoxybenzoin. Benzyl-phenyl-methyl carbinol loses water with greater difficulty than stilbene hydrate (*Hell*, Ber. 37, 456; *Klages*, Ber. 37, 1450).

**Desoxybenzoin**, *benzyl-phenyl ketone*,  $C_6H_5CH_2COC_6H_5$ , m.p.  $60^\circ$ , b.p.  $314^\circ$ , is obtained by distilling a mixture of calcium benzoate and calcium  $\alpha$ -toluate, by the action of  $\alpha$ -toluyl chloride on benzene in the presence of aluminium chloride, by reduction of benzoin with zinc and hydrochloric acid (*Meyer*, Ber. 21, 1296; *Stobbe*, Ber. 35, 912), by the action of zinc and hydrochloric acid, or of hydriodic acid on chlorobenzil or benzil (*Japp*, J. 63, 770; *Thiele*, Ann. 319, 252), and by heating monobromostilbene with water to  $180-190^\circ$ . One of the H atoms of the methylene group of desoxybenzoin can readily react with sodium and be replaced by alkyl, but not the second (*Meyer*, Ber. 21, 1297; *Buddeberg*, Ber. 23, 2072). Methyl-, isobutyl- and cetyl-desoxybenzoin melt at  $58^\circ$ ,  $78^\circ$ , and  $76^\circ$ , respectively (*Sudborough*, Ber. 25, 2237). Allyl-desoxybenzoin, see *Danilow*, J. Russ. Phys.-Chem. Soc. 51, 128, where doubly-substituted desoxybenzoins are also dealt with. Desoxybenzoin-oxime melts at  $98^\circ$ . Isonitroso-desoxybenzoin, obtained by the action of nitrogen trioxide, is identical with  $\alpha$ -benzil-monoxime. Desoxybenzoin gives dibenzyl when reduced with hydriodic acid; see also stilbene hydrate.

**Formyl-desoxybenzoin** is obtained from desoxybenzoin by condensation with ethyl formate in the presence of sodium ethylate. It occurs in two desmotropic forms, an enol-keto form,  $C_6H_5 \cdot C=CHOH$ , m.p.  $76-80^\circ$ , yellow in colour, and

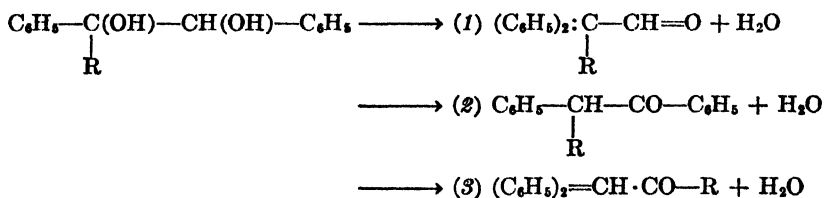
an aldo-enol form,  $C_6H_5 \cdot C=CHO$ , m.p.  $112-113^\circ$ , which is colourless (*Wislicenus*, Ann. 379, 252).

When desoxybenzoin is nitrated, *o*-nitrodesoxybenzoin,  $C_6H_4(NO_2)CH_2COC_6H_5$ , is formed. When this compound is reduced,  $\alpha$ -phenyl-indole is formed,

$C_6H_5 \cdot \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{CC}_6H_5$ . Desoxytoluin,  $CH_3C_6H_4CH_2COC_6H_5$ , desoxyanisoin,

$CH_3OC_6H_4CH_2COC_6H_5OCH_3$ , are obtained from the corresponding tolanes (*Buttenberg*, Ann. 279, 335, 339). By the action of thiocarbonyl chloride or carbon disulphide and caustic potash on desoxybenzoins, *desaurins* are obtained. These form fiery golden-yellow crystals, which dissolve in sulphuric acid with a violet colour. The constitution of these compounds is still unknown, but possibly the simplest desaurin has the composition  $C_6H_5COC(CS)C_6H_5$  (*Wachter*, Ber. 25, 1731; *Sudborough*, Ber. 25, 2239; cf. *Apitzsch*, Ber. 37, 1599). **Mono- and polyhydroxy-desoxybenzoins**, see Mo. 26, 927; *Chapman*, J. 123, 404.

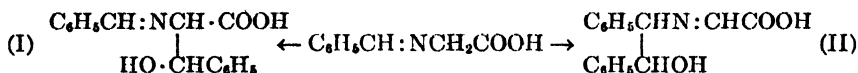
**Hydrobenzoin**, toluylene glycol,  $C_6H_5CH(OH)CH(OH)C_6H_5$ , has two asymmetric carbon atoms, and occurs in two optically inactive forms (*Anschütz*, Ann. 259, 100), hydrobenzoin, m.p.  $134^\circ$ , and *iso*-hydrobenzoin, m.p.  $119^\circ$ . The latter has been resolved into two optically active components. Both forms are produced, together with benzyl alcohol, by the action of zinc and hydrochloric acid on benzaldehyde, or by reduction of benzaldehyde with sodium amalgam. They can also be obtained by electrolytic reduction of benzaldehyde (*Kauffmann*, Z. Elektrochem. 2, 365). They can also be obtained from stilbene dibromide or dichloride, if this is converted by means of silver acetate or benzoate into the ester of hydrobenzoin, which is then hydrolysed with alcoholic ammonia. With potassium acetate it is chiefly *iso*-hydrobenzoin that is formed, but with silver oxalate, mainly hydrobenzoin. Hydrobenzoin is obtained together with a little *iso*-hydrobenzoin by the reduction of benzoin with sodium amalgam (method of preparation) (*Weise*, Ann. 248, 36). Hydrobenzoin is difficultly soluble in water. It crystallises in rhombic tablets and sublimes without decomposition. Its diacetyl ester, m.p.  $134^\circ$ , is obtained by the action of zinc dust on benzaldehyde and acetyl chloride (*Paal*, Ber. 16, 636). *iso*-Hydrobenzoin is more easily soluble in water, and crystallises in prisms containing water of crystallisation, but which soon effloresce. Its diacetyl ester is dimorphous, one form crystallising in leaflets, m.p.  $118^\circ$ , the other in prisms, m.p.  $106^\circ$ . By crystallisation from ether it is possible to resolve *iso*-hydrobenzoin into enantiomorphous dextro- and laevo-rotatory crystals (*Erlenmeyer, Jr.*, Ber. 30, 1531). Both give diphenylacetaldehyde,  $(C_6H_5)_2CH \cdot CHO$ , when acted upon with sulphuric acid. Mono-substituted hydrobenzoins react according to the conditions and the nature of the substituents, either in the same way (1) or with formation of desoxybenzoins (2) or  $\alpha, \alpha'$ -diphenyl-ketones (3):



(*Tiffeneau*, Bull. [4], 33, 195; *Roger*, Ber. 62, 272). Both hydrobenzoins give benzaldehyde when oxidised with chromic acid or permanganate, and benzoin with nitric acid (*Auwers*, Ber. 24, 1776). Both react with phosphorus pentabromide forming stilbene dibromide,  $C_6H_5CHBr \cdot CHBrC_6H_5$ , m.p.  $237^\circ$ , which can also be obtained by the action of bromine on stilbene or dibenzyl. If stilbene

is brominated, in addition to  $\alpha$ -stilbene dibromide, m.p.  $237^\circ$ , a more readily soluble  $\beta$ -stilbene dibromide, m.p.  $110^\circ$  is obtained. This is produced in better yield from isostilbene, and on heating is converted into the higher melting form. The latter is converted by alcoholic potash into a liquid monobromostilbene, whilst the  $\beta$ -dibromide gives a solid monobromostilbene (*First*, Ber. 28, 2693). With phosphorus pentachloride both hydrobenzoin give  $\alpha$ - and  $\beta$ -stilbene dichloride, m.p.  $192^\circ$ , and  $93^\circ$ , respectively. The  $\alpha$ -compound can also be obtained from stilbene by the action of chlorine in chloroform solution. On heating to  $200^\circ$ , the  $\beta$ -form is converted into the  $\alpha$ -form.

Diphenyl-hydroxyethylamine,  $C_6H_5CH(OH)CH(NH_2)C_6H_5$ , m.p.  $163^\circ$ , and *iso*-diphenyl-hydroxyethylamine, m.p.  $129^\circ$ , are obtained together by the reduction of benzoin oxime, and by the action of benzaldehyde on benzylamine. It can also be obtained, together with phenyl- $\alpha$ -aminolactic acid (p. 420) by the action of glycocoll on benzaldehyde. The latter reaction is explained by the condensation of benzaldehyde with benzyldine-glycocoll in two directions, according to the following scheme:



(I) splits into benzaldehyde and phenyl-aminolactic acid, while (II) splits into glyoxylic acid and diphenylhydroxy-ethylamine. The two diastereoisomeric diphenylhydroxy-ethylamines can be resolved by means of their *benzylidene* compounds. Both are converted into *iso*-hydrobenzoin by nitrous acid. Both bases have been resolved into optically active components (*Read*, J. 1927, 910; 1929, 2305). The diphenylhydroxy-ethylamine with  $[\alpha]_D = 10^\circ$ , apparently has the configuration of internally compensated hydrobenzoin, *iso*-diphenylhydroxy-ethylamine with  $[\alpha]_D = 133.5^\circ$ , has the configuration of *iso*-hydrobenzoin. The quaternary ammonium bases obtained by exhaustive methylation of diphenylhydroxy-ethylamines,  $C_6H_5CH(OH) \cdot CH(C_6H_5)N(CH_3)_3OH$ , are decomposed on heating with water into trimethylamine, water, and diphenyl-ethylene oxide,

$C_6H_5CH \cdot O \cdot CHC_6H_5$ , m.p.  $69^\circ$ , and *iso*-diphenyl-ethylene oxide, m.p.  $42^\circ$  (*Rabe*, Ber. 43, 884).

Diphenylethylene-diamine, stilbene-diamine,  $C_6H_5CH(NH_2)CH(NH_2)C_6H_5$ , m.p.  $91^\circ$ , is obtained by reduction of benzil dioxime with sodium and alcohol. It is resolved into two optically active components by crystallisation of its bitartrate (*First*, Ber. 28, 3167). Tetraphenyl-diethylene-diamine, or tetraphenylpiperazine,  $NH[CH(C_6H_5) \cdot CH(C_6H_5)]_2NH$ , is obtained by reduction of diphenyl-dinitroethane (p. 559) or diphenyldinitroethylene (p. 561) with zinc dust and acetic acid.

The dianhydride of an *o,o'*-dihydroxyhydrobenzoin,  $O \cdot C_6H_4CH \cdot CHC_6H_4O$ , has been obtained in two forms by reduction of salicylaldehyde with zinc dust and acetic acid. They melt at  $68^\circ$  and  $114^\circ$  (*Harries*, Ber. 24, 3175).

**Benzoin**, *benzoyl-phenyl carbinol*,  $C_6H_5CH(OH)COC_6H_5$ , m.p.  $134^\circ$ , is obtained by the oxidation of hydrobenzoin with nitric acid, and by the condensation of two molecules of benzaldehyde in aqueous-alcoholic solution, in the presence of potassium cyanide.

These reactions (for theory see *Chalanay*, Ber. 25, 293; *Smith*, Ber. 26, 60), which will also take place in the absence of water to give an addition product of sodium cyanide and benzaldehyde, which slowly changes to benzoin (*Morton*, Am. 52, 2031), also apply to other aromatic aldehydes (*Ekecrantz*, Ark. Kemi. Mineral. Geol. 3, No. 13; C. 1908, II, 1689). The ketonic-alcohols thus obtained, such as *anisoin*,  $CH_3O \cdot C_6H_4CH(OH)COC_6H_5 \cdot OCH_3$ , from anisaldehyde, *cuminoin* from cuminal, *etc.*, reduce Fehling's solution, becoming oxidised to the corresponding benzils.

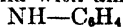
*d*- and *l*-Benzoin are obtained by the action of phenyl magnesium bromide on *d*- and *l*-mandelamides (*Wren*, J. 95, 1583), and by the resolution of racemic

benzoin by means of *l*- and *d*-( $\alpha$ -phenylethyl)-semicarbazide (Hopper, J. 1928, 2483).

Benzoin is oxidised to benzaldehyde and benzoic acid by chromic acid, and to benzil by nitric acid. It is reduced to hydrobenzoin by sodium amalgam, and to desoxybenzoin by zinc and hydrochloric acid. On boiling with dilute caustic potash benzoin is unaffected if air is excluded, but if a current of air is passed through a large part of it is converted into benzoic acid (p. 556). When heated with concentrated alkali, benzoin is converted partially into benzyl alcohol and benzoic acid, and on longer treatment, hydrobenzoin, stilbene hydrate, etc., are formed (Knoevenagel, Ber. 35, 1982). On treatment with acids decomposition to diphenylacetic acid can occur (Lachman, Am. 45, 1529).

**Benzoin-hydrazone**, m.p. 75° (Curtius, J. pr. [2], 52, 124); **semicarbazone**, m.p. 206° (Biltz, Ann. 339, 257); **phenylhydrazone**, m.p. 158° and 106° (Smith Am. 16, 107);  $\alpha$ -**oxime**, m.p. 152°,  $\beta$ -**oxime**, m.p. 99°. Acetyl- $\beta$ -benzoin oxime is converted into acetyl- $\beta$ -benzil oxime by oxidation with chromic acid, and this determines its configuration (Werner, Ber. 38, 69). Benzoin is alkylated by treatment with alcohols and hydrogen chloride, or silver oxide and alkyl halides: **methyl-benzoin**,  $C_6H_5CH(OCH_3)COC_6H_5$ , m.p. 50°; **ethyl-benzoin**, m.p. 62°; **isopropyl-benzoin**, m.p. 72-75° (Fischer, Ber. 26, 2412; Lander, Proc. 16, 6).

The chloride ester of benzoin, **desyl\* chloride**,  $C_6H_5CHClCOC_6H_5$ , m.p. 68°, is obtained by warming benzoin with thionyl chloride (Schroeter, Ber. 42, 2348); **desyl bromide**,  $C_6H_5CHBrCOC_6H_5$ , m.p. 55°, is obtained by acting on desoxybenzoin with bromine. It reacts with aniline giving **desyl anilide**, benzoin-anilide,  $C_6H_5CH(NHC_6H_5)COC_6H_5$ , m.p. 99°. This compound can also be obtained by heating aniline with benzoin. On heating with aniline hydrochloride to 160°, on the other hand, **benzoinanil-anilide**,  $C_6H_5CH(NHC_6H_5)C(:NC_6H_5)C_6H_5$ , m.p. 125°, is formed, and with aniline and zinc chloride at higher temperatures, **di-**



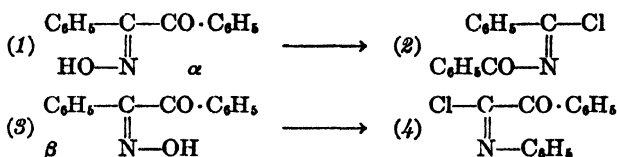
**phenyl-undole**,  $C_6H_5C \equiv C \cdot C_6H_5$ , is formed (Bischler, Ber. 26, 1336; Japp, Ber. 26, 2640). **Benzoin-*p*-toluidide**,  $C_6H_5CH(NHC_6H_4 \cdot CH_3)COC_6H_5$ , m.p. 145°, is produced by the condensation of benzaldehyde and benzylidene-toluidine by means of potassium cyanide (Miller, Ber. 29, 1736; cf. on the other hand, pp. 272, 413 and Miller, Ber. 31, 2699). Benzoin condenses with *o*-diamines giving **dihydroquinoxalines**, and with urea and thiourea (Wislicenus, Ann. 248, 8) to give **glyoxaline** derivatives. It also condenses with nitriles forming **oxazole**-derivatives. For condensation products of benzoin with acetone, see Smith, Ber. 26, 65, with pinacoline, Boon, J. 97, 1256; and with acetophenone, p. 574.

**Benzil**, or **dibenzoyl**, **diphenyl-glyoxal**,  $C_6H_5COCOC_6H_5$ , m.p. 90°, b.p. 347°, forms beautiful yellow prisms. It is the most readily accessible  $\alpha$ -diketone. It is obtained by boiling stilbene bromide with water and silver oxide, and is obtained from benzoin by warming with concentrated nitric acid; cf. also isobenzil, p. 569.

With hydrazine hydrate, benzil gives **hydrazibenzil**,  $C_6H_5C(N_2H_2) \cdot C(C_6H_5)_2$ , and **bishydrazibenzil**,  $C_6H_5C(N_2H_2) \cdot C(N_2H_2)C_6H_5$ , which on oxidation give **azibenzil**,  $C_6H_5C(N_2) \cdot C(C_6H_5)_2$ , and **bisazibenzil**,  $C_6H_5C(N_2) \cdot C(N_2)C_6H_5$ , respectively (Curtius, Ber. 29, 775). When heated in indifferent solvents, azibenzil breaks down into nitrogen and **diphenylketene** (p. 554) (Schroeter, Ber. 42, 2346), and **bis-azibenzil** into nitrogen and toluene. **Benzil monosemicarbazone**, m.p. 175°, when heated with alcohol, loses water and becomes diphenylhydroxytriazine. **Benzil disemicarbazone**, m.p. 244°, see Biltz, Ann. 339, 243. **Benzil-osazone**,  $(C_6H_5)_2C_2(NNHC_6H_5)_2$ , m.p. 225°, gives triphenylosotriazole on heating (Pickel, Ann. 232, 230; Purgotti, Gazz. 22, 11, 611). An isomeric form of benzil-osazone, m.p. 208°, is obtained by the action of iodine and sodium ethylate or of air, on an alkaline-alcoholic solution of benzal-phenylhydrazone. Derivatives of this osazone are formed in a similar way. When heated above the melting point it is converted into the higher melting form (Ingle, Proc. 1895, 111; Biltz, Ber. 35, 3519; Ann. 305, 170; 324, 310; Challaway, Proc. 24, 175).

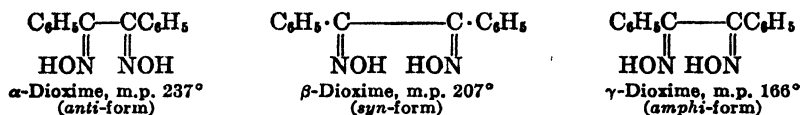
\* Desyl =  $C_6H_5CO-CH(C_6H_5)-$ .

By the action of 1 mol. of hydroxylamine on benzil, two isomeric benzil monoximes,  $\alpha$ -m.p.  $134^\circ$ ,  $\beta$ -m.p.  $113^\circ$ , are formed. The  $\alpha$ - is converted into the  $\beta$ -monoxime by the action of hydrogen chloride and glacial acetic acid, by heating to the melting point, or heating with alcohol to  $100^\circ$ . With hydroxylamine,  $\alpha$ - and  $\beta$ -benzil-dioxime are formed (*Auwers*, Ber. 22, 540, 709). When heated, both monoximes break down into benzonitrile and benzoic acid. Benzoin-oxime is reduced by stannous chloride and hydrochloric acid to desylamine,  $C_6H_5CH(NH_2)COC_6H_5$ , m.p.  $109^\circ$  (*Paschorr*, Ber. 35, 2740). For the action of phenylhydrazine, see *Auwers*, Ber. 26, 792; *Minunni*, Gazz. 22, II, 183. The behaviour of the benzil monoximes as regards the Beckmann transformation is interesting.  $\alpha$ -Monoxime (1) gives benzoyl-benzimide-chloride (2), which readily decomposes into benzonitrile and benzoyl-chloride; the  $\beta$ -monoxime (3), on the other hand, gives benzoyl-formanilide-chloride (4) (*Beckmann*, Ann. 296, 279; *Werner*, Ber. 37, 4295):

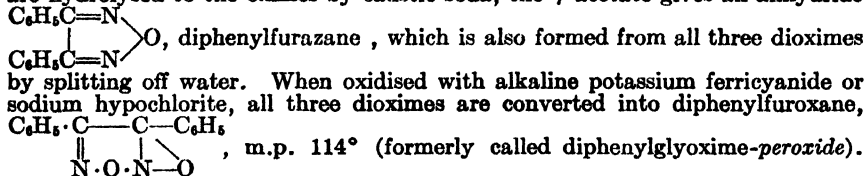


In the first case, the hydroxyl radical has changed places with the benzoyl radical, and in the second with the phenyl radical. Since, according to the work of *Meisenheimer*, the Beckmann transformation is in general a "trans"-exchange, this makes the  $\alpha$ -monoxime the *anti*-benzoyl form, and the  $\beta$ -monoxime the *syn*-benzoyl form. There is evidence for this in the fact that triphenyl-isoxazole gives benzoyl- $\beta$ -benzil-monoxime when ozonised (*Meisenheimer*, Ber. 54, 3206).

By the action of 2 mols. of hydroxylamine on benzil, two benzil-dioximes are formed,  $\alpha$ -m.p.  $237^\circ$ ,  $\beta$ -m.p.  $207^\circ$ . A third,  $\gamma$ -dioxime, m.p.  $166^\circ$ , is obtained from  $\beta$ -benzil-monoxime. The most stable is the  $\beta$ -dioxime; the other two readily pass into this one. Under certain conditions the  $\gamma$ -dioxime will pass into the  $\alpha$ -form (*Beckmann*, Ann. 274, 33). *Meisenheimer* ascribes the following formulae to the three dioximes:



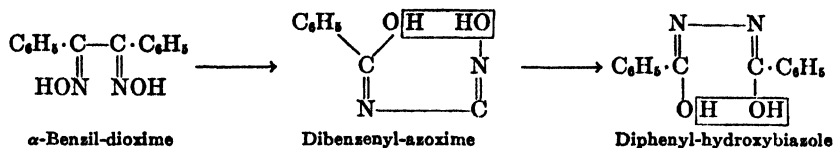
With acid anhydrides, three different esters are formed: benzil-dioxime-diacetate,  $\alpha$ -m.p.  $148^\circ$ ,  $\beta$ -m.p.  $124^\circ$ ,  $\gamma$ -m.p.  $114^\circ$ . While the  $\alpha$ - and  $\beta$ -diacetates are hydrolysed to the oximes by caustic soda, the  $\gamma$ -acetate gives an anhydride



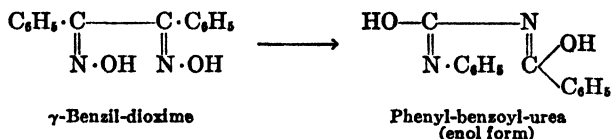
When this is rapidly heated it passes into phenyl isocyanate, apparently with primary dissociation into 2 mols. of benzonitrile-oxide (p. 313) (*Wiand*, Ber. 42, 806).

In this case too, a satisfactory picture of the behaviour of the three dioximes with regard to the Beckmann transformation is given by *Meisenheimer's* theory that the oxime hydroxyl preferentially changes places with the group in the *trans*-position (*Meisenheimer*, Ber. 54, 3206; 57, 276).

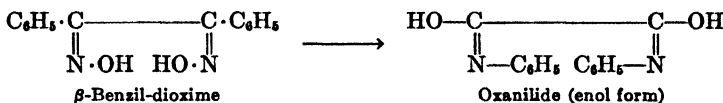
I.  $\alpha$ -Benzil-dioxime, when acted upon by phosphorus pentachloride gives chlorides, of which first the one and then the other hydroxide group changes places, which can be converted into the anhydrides dibenzoyl-azoxime and diphenyl-hydroxybiazole:



II.  $\gamma$ -Benzil-dioxime also gives dibenzenyl-azoxime in the first stage, which undergoes a double place exchange with formation of phenyl-benzoyl-urea:



III. The  $\beta$ -dioxime gives oxanilide, by means of a double place exchange:



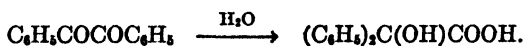
The  $\gamma$ -diacetate readily passes into diphenylfurazane, which, according to the above scheme, would be expected from the  $\beta$ -diacetate. For this anomaly, see *Meisenheimer*, Ber. 57, 276.

The analogy between the benzil-dioximes and the osazones of ethyl dioxysuccinate (p. 151) is interesting. The latter occurs in three isomeric forms, of which one is stable, and the other two labile, so that it is likely that the same type of isomerism underlies both sets of compounds (*Anschütz*, Ber. 28, 64).

When benzil is heated with aniline to 200°, *benzil-monoanil*,  $\text{C}_6\text{H}_5\text{CO} \cdot \text{C}(\text{NC}_6\text{H}_5)\text{C}_6\text{H}_5$ , m.p. 106° is formed. With phosphorus pentoxide this gives *benzil-dianil*,  $\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_5)\text{C}(\text{NC}_6\text{H}_5)\text{C}_6\text{H}_5$ , m.p. 142° (*Siegfeld*, Ber. 25, 2600; *Lachowicz*, Mo. 14, 279). As an *o*-diketone, benzil is capable of entering into reactions which give rise to heterocyclic rings. It condenses with ethylene diamine to give a dihydropyrazine derivative. With ortho-diamines it gives quinoxalines, and with *o*-aminodiphenylamine it gives a so-called stilbazonium base. With urea and thiourea it gives *ureides* and *diureides*, and with semicarbazide it gives hydroxy-diphenyltriazine, etc. It is converted into desoxybenzoin by reduction with hydriodic acid, and it is oxidised to benzoic acid by chromic acid. On standing with potassium cyanide and alcohol it undergoes fission into benzoic acid and benzaldehyde.

For the condensation of benzil with acetone, diethyl malonate, ethyl acetoacetate, laevulinic acid, etc., see *Japp*, J. 67, 132; J. 69, 736; Proc. 1895, 146; J. 71, 123; 83, 279; Proc. 21, 152; J. 87, 673.

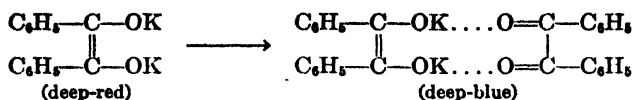
The conversion of benzil into benzoic acid by fusion with caustic potash, or boiling with alcoholic potash is important:



For this reaction it is necessary to use equimolecular quantities of benzil and alkali. At first an addition compound is formed, which with water breaks down into its components again, but on standing with excess alkali, or warming, it is converted into benzoic acid (*Scheuing*, Ber. 56, 252; *Evans*, Am. 52, 252). Benzoic acid is formed as a by-product; the quantity of it formed depends on the amount of water present (*Lachman*, Am. 46, 779).

Benzil gives a deep red di-potassium compound with metallic potassium. This compound will combine with a further molecule of benzil giving a quinone-like product which is deep blue in colour:



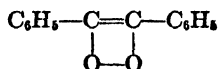


The di-potassium compound is affected by oxygen and moisture. Its constitution as a stilbene-diol-dipotassium follows from its reaction with acetic anhydride, when it gives stilbene-diol-diacetate (*Staudinger*, *Helv.* 5, 703).

With phosphorus pentachloride, benzil gives chlorobenzil,  $\text{C}_6\text{H}_5\text{COCCl}_2\text{C}_6\text{H}_5$ , m.p.  $61^\circ$ , and further toluene-tetrachloride,  $\text{C}_6\text{H}_5\text{CCl}_2\text{CCl}_2\text{C}_6\text{H}_5$ , m.p.  $163^\circ$ . The latter can be obtained synthetically by heating benzotrichloride with copper. On heating with glacial acetic acid or sulphuric acid it gives benzil.

By nitration, benzil yields: 3,3'-dinitrobenzil, m.p.  $132^\circ$ ; by stronger action, 3,5,3',5'-tetranitrobenzil, m.p.  $179^\circ$  (*Chattaway*, *J.* 1927, 577). 2,4-Dinitrobenzil, m.p.  $105^\circ$ , is obtained from 2,4-dinitro-stilbene (*Bishop*, *J.* 121, 2364).

For chlorobenzils, phenylbenzils, hydroxybenzils, and their derivatives see *Gomberg*, *Am.* 51, 2238; *Asahina*, *Ber.* 62, 171; *Brass*, *Ber.* 63, 2617. Although benzil itself is yellow in colour, some of the hydroxy- and methoxy-benzils are pure white. Many of them dissolve giving a yellow solution. The explanation of this phenomenon is thought to be connected with the supposed presence of peroxide-like linkages, which possibly also explains the lack of reactivity of these compounds towards ketone reagents:



(*Schonberg*, *Ber.* 55, 1174, 3753; *Marsh*, *J.* 127, 1633). Optical experiments have not, however, confirmed this view (*Burawoy*, *Ber.* 65, 1068).

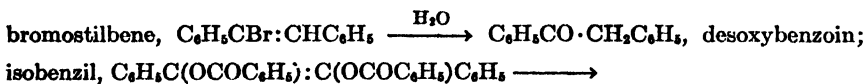
Methoxybenzils can be converted into phenanthraquinone derivatives by means of aluminium chloride (*Brass*, *Ber.* 63, 2613, 2617).

Anisil,  $(\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4\text{CO})_2$ , m.p.  $133^\circ$ , and cuminil  $(\text{C}_6\text{H}_7 \cdot \text{C}_6\text{H}_4\text{CO})_2$ , m.p.  $84^\circ$ , are obtained by the action of nitric acid on anisoin and cuminoin (p. 564) in just the same way as benzil is obtained from benzoil. Anisil and a hexamethoxybenzil,  $[(\text{CH}_3\text{O})_2\text{C}_6\text{H}_2\text{CO}]_2$ , m.p.  $189^\circ$  are also obtained by alkaline reduction of anisamide and trimethylgallamide (*Marx*, *Ann.* 263, 249). These compounds form anisilic acid, cuminilic acid, and hexamethoxybenzilic acid when fused with potash (p. 556).

The osazones of various substituted benzils, such as salicil, cuminil, anisil, piperil, are obtained in a similar manner to benzil-osazone, by the action of atmospheric oxygen on alkaline-alcoholic solutions of the phenylhydrazones of the corresponding aldehydes (salicyl-aldehyde, piperonal, etc.) (*Ann.* 308, 1).

*p,p'*-Tetramethyldiamino-benzil,  $(\text{CH}_3)_2\text{NC}_6\text{H}_4 \cdot \text{CO} \cdot \text{COC}_6\text{H}_4\text{N}(\text{CH}_3)_2$ , m.p.  $198^\circ$ , is obtained by warming oxalyl chloride with excess of dimethylaniline (*Staudinger*, *Ber.* 42, 3487).

2. ALCOHOLIC DERIVATIVES OF STILBENE. These compounds are unknown in the free state. When their esters are hydrolysed the isomeric ketones are usually obtained (*cf.* phenyl-vinyl alcohols, p. 456):



However, benzoin reacts very often as if it were an unsaturated glycol of the formula,  $\text{C}_6\text{H}_5\text{C}(\text{OH}):\text{C}(\text{OH})\text{C}_6\text{H}_5$ , *e.g.*, with mercaptans it gives ethers of the corresponding dithioglycol: dithioethyl-stilbene,  $\text{C}_6\text{H}_5\text{C}(\text{SC}_2\text{H}_5):\text{C}(\text{SC}_2\text{H}_5)\text{C}_6\text{H}_5$ , m.p.  $105^\circ$  (*Posner*, *Ber.* 35, 506).

Monochlorostilbene,  $\text{C}_6\text{H}_5\text{CH}:\text{CClC}_6\text{H}_5$ , is an oil, b.p.  $320\text{--}324^\circ$ . It is obtained by the action of phosphorus pentachloride on desoxybenzoin, and by the action of alcoholic potash on stilbene dichloride. When boiled with glacial acetic acid it is converted into an isomeric form m.p.  $54^\circ$ , and with chlorine and bromine it gives chlorostilbene dichloride,  $\text{C}_6\text{H}_5\text{CCl}_2 \cdot \text{CHClC}_6\text{H}_5$ , m.p.  $103^\circ$ , and chloro-

**stilbene dibromide**, m.p. 127° (*Sudborough*, J. 71, 218). **Methyl chlorostilbene** is obtained in a similar way from methyl-desoxybenzoin. It has the formula  $C_6H_5C(CH_3):CClC_6H_5$ , and is an oil, melting at 118° (*Sudborough*, Ber. 25, 2237; Chem. News 72, 188). **Monobromostilbene**, m.p. 31°, is obtained by the action of alcoholic potash on  $\beta$ -stilbene-dibromide (p. 564) while  $\alpha$ -stilbene dibromide gives a liquid isobromostilbene, m.p. 19°. On heating the liquid form turns into the solid. Isobromostilbene gives the liquid isostilbene when reduced with zinc and alcohol (p. 560).

**POLYNITROSTILBENES** are obtained by condensation of polynitrotoluenes with aromatic aldehydes (*Thiele*, Ber. 34, 2842). **2,4-Dinitrostilbene**, m.p. 143–145° (*Pastak*, Bull. [4], 39, 72).

**Diacetoxy-stilbene**, stilbene-glycol diacetate,  $C_6H_5C(OCOCH_3):C(OCOCH_3)C_6H_5$ ,  $\alpha$ -form m.p. 153°,  $\beta$ -form m.p. 110°, is obtained by the reduction of benzil by means of zinc dust and acetic anhydride and sulphuric acid (*Thiele*, Ann. 306, 142).

**Isobenzil**, stilbene-glycol dibenzoate,  $C_6H_5C(OCOC_6H_5):C(OCOCH_3)C_6H_5$ , m.p. 156°, is obtained by the action of sodium on an ether solution of benzoyl chloride. When hydrolysed with alkali it is broken down into benzoic acid and benzoin (*Klinger*, Ber. 24, 1264).

**Dichlorostilbene**, tolane-dichloride,  $C_6H_5CCl:CClC_6H_5$ , is known in two forms,  $\alpha$ -m.p. 143°,  $\beta$ -m.p. 63°; both are obtained by the addition of chlorine to tolane, or by the reduction of tolane tetrachloride with iron and acetic acid. They are also formed by the action of caustic potash on chlorostilbene dichloride (see above). In a similar way chlorostilbene dibromide yields **chlorobromostilbene**,  $C_6H_5CCl:CBrc_6H_5$ , m.p. 174°. **Dibromostilbene**,  $\alpha$ -m.p. 208°,  $\beta$ -m.p. 64°, is obtained by the action of bromine on tolane. For  $p,p'$ -dihydroxy-derivatives of dichlorostilbene and their conversion into methylene-quinones of the dibenzyl series, see p. 340 and *Zincke*, J. pr. [2], 59, 228; Ann. 325, 67.

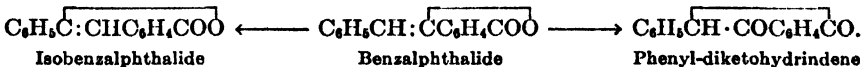
**3. CARBOXYLIC ACIDS OF THE DIBENZYL GROUP.** These may be considered under two heads: (a) those in which the carboxyl group is in the phenyl radical, and (b) those in which it is in the side-chain; these are diphenylated fatty acids. A series of *o*-carboxylic acids obtained by condensations involving phthalic anhydride belong to the first group.

(a) **Dibenzyl-*p*-monocarboxylic acid**, m.p. 173–174°, is obtained by condensation with oxalyl chloride in the presence of aluminium chloride (*Liebermann*, Ber. 45, 1186). **Dibenzyl-*o,o'*- and *p,p'*-dicarboxylic acid**,  $COOHC_6H_4CH_2:CH_2C_6H_4COOH$ , m.p. 231°, and over 320°, respectively, are produced by the oxidation of *o*- and *p*-toluic acids with potassium persulphate (*Fischer*, Ber. 37, 3215). The latter can also be obtained from dibenzyl and oxalyl chloride, together with the monocarboxylic acid.

**Desoxybenzoin-*o*-carboxylic acid**,  $C_6H_5\cdot CH_2\cdot COC_6H_4COOH (+H_2O)$ , m.p. 75°, is obtained by boiling the corresponding lactone, **benzylidene-phthalide**,

$C_6H_5CH:CC_6H_4COO$ , m.p. 99°, with alkali. The latter is obtained by condensation of phthalic anhydride and phenylacetic acid, with loss of carbon dioxide.

Benzalphthalide can be converted into **isobenzalphthalide**,  $C_6H_5C:CHC_6H_4COO$ , m.p. 91°, via nitrobenzalphthalide. Isobenzalphthalide is the lactone of  $\beta$ -desoxybenzoin-*o*-carboxylic acid,  $C_6H_5CO\cdot CH_2C_6H_4COOH$ , m.p. 163°. The latter can also be obtained from homophthalic anhydride (p. 393), benzene, and aluminium chloride (*Graebe*, Ber. 37, 377), as well as by decomposition of 2-phenylhydrindone with caustic soda. Benzalphthalide undergoes another transformation under the influence of sodium ethylate, when the sodium salt of 2-phenyl-diketohydrindene (p. 600) is formed:



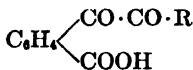
$$\begin{array}{c} \text{N} \\ \parallel \\ \text{N} - \text{NH} \\ | \\ C_6H_5CH_2CC_6H_4CO \end{array}$$

**Benzyl-phthalazone**,  $C_6H_5CH_2CC_6H_4CO$ , is obtained by the action of hydrazine on benzalphthalide. It is converted into **benzyl-phthalimidine** by reduction with

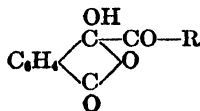
glacial acetic acid and zinc. The latter has the formula,  $C_6H_5CH_2 \cdot \overline{CHC_6H_4CO \cdot NH}$ , and m.p. 137°. It is also obtained by the reduction of benzal-phthalimidine (Bromberg, Ber. 29, 1434; Gabriel, Ber. 29, 2743). For homologues of benzal-phthalide, see Bothmann, Ber. 32, 1104, etc.

When phthalic anhydride is heated with homophthalic acid and sodium acetate, desoxybenzoin-*o,o'*-dicarboxylic acid,  $COOH \cdot C_6H_4CH_2COC_6H_4COOH$ , m.p. 239°, is formed (Ephraim, Ber. 24, 2820).

Reduction of desoxybenzoin-mono- and -di-carboxylic acids gives rise to di-benzyl-mono- and -di-carboxylic acids. By oxidation of *o*-desoxybenzoin-carboxylic acid, benzil-*o*-carboxylic acid,  $C_6H_5COCOC_6H_4COOH$ , is obtained. It exists in two forms, a yellow form, m.p. 141°, and a white form, m.p. 125–130° (Graebe, Ber. 23, 1344; Auwers, Ber. 23, 2079; Gabriel, Ber. 29, 2745; Soch, J. Phys. Chem. 2, 376). This isomerism is a special type of keto-hydroxylactone isomerism, as found in the esters and chlorides of *o*-benzoyl-benzoic acid (p. 522) (Hantzsch, Ber. 49, 213)



(yellow keto-form)



(colourless hydroxylactone-form)

Benzil-*o,o'*-dicarboxylic acid, m.p. 273°, is known only in the colourless hydroxy-lactone form,  $\overline{OOC_6H_4C(OH)COH \cdot C_6H_4 \cdot COO}$ , which gives a diacetyl derivative with acetyl chloride. However, it forms esters and salts of both forms. This compound is obtained by the oxidation of chrysoquinone, chrysoketone, or  $\alpha$ -naphthol (Graebe, Ann. 311, 264; Dischendorfer, Mo. 50, 97). It is also obtained by the action of glacial acetic acid and zinc dust on phthalic anhydride, followed by oxidation of the product, and by oxidation of:

Diphthalyl,  $\overline{OOC_6H_4C : C_6H_4COO}$ , m.p. 334°. This can be obtained by heating phthalonic acid (p. 440), by condensation of phthalide (p. 376) and phthalic anhydride with sodium acetate, or by the condensation of 2 mols. of the ester of phthalaldehydic acid with potassium cyanide, a reaction resembling the formation

of benzoin. Tetramethoxy-diphthalyl,  $\overline{OOC_6H_4(OCH_3)_2C : C_6H_4(OCH_3)_2COO}$ , is obtained in a similar way by condensation of ethyl opianate (p. 381).

Dithiodiphthalyl,  $\overline{SOC_6H_4C : C_6H_4COS}$ , greenish-yellow needles, m.p. 333°, see Ber. 31, 2646.

Dihydrodiphthalyl-diimide,  $\overline{NH \cdot COC_6H_4CH \cdot CHC_6H_4CO \cdot NH}$ , m.p. 284° (decomp.), a compound isomeric with indigo white, is obtained by condensation of phthalaldehydic ester with methyl alcoholic ammonia (cf. Gabriel, Ber. 29, 2745).

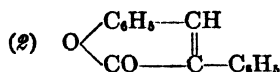
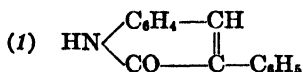
Hydrodiphthalyl-lactonic acid,  $\overline{HOCC_6H_4CH_2 \cdot CHC_6H_4COO}$ , m.p. 198°, is obtained by heating homophthalic acid to 230° (Graebe, Ber. 31, 376).

(b) Dibenzyl-carboxylic acid,  $\alpha$ -phenyl-hydrocinnamic acid,  $\alpha, \beta$ -diphenyl-propionic acid, benzyl-phenylacetic acid,  $C_6H_5CH_2CH(C_6H_5)COOH$ , is obtained by reduction of phenylcinnamic acid. It occurs in three isomeric forms, with m.p. 95°, 89°, and 82° (b.p. 335°) (Miller, Ber. 25, 2017). Its nitrile is obtained by the benzoylation of benzyl cyanide.  $\alpha$ -Phenyl-*o*-aminohydrocinnamic acid, m.p. 148°, has been obtained by the reduction of  $\alpha$ -phenyl-*o*-nitrocinnamic acid (Bakunin, Gazz. 25, I, 137). It readily passes into the lactam,  $\beta$ -phenylhydro-

carbostyryl,  $C_6H_5 \begin{cases} CH_2 - CHC_6H_5 \\ NH - CO \end{cases}$ , m.p. 174°.  $\alpha, \beta$ -Diphenylvaleric acid,  $C_6H_5 \cdot$

$CH(C_6H_5)CH(C_6H_5)COOH$ , m.p. 178°; its nitrile, m.p. 115°, is obtained by the addition of ethyl magnesium iodide to  $\alpha$ -phenyl-cinnamyl nitrile.

**Stilbene-carboxylic acid,  $\alpha$ -phenylcinnamic acid**,  $C_6H_5CH:C(C_6H_5)COOH$ , m.p.  $172^\circ$ , is obtained by the condensation of benzaldehyde with phenylacetic acid; allo- $\alpha$ -phenylcinnamic acid is formed at the same time (m.p.  $137^\circ$ ) (*Bakunin*, *Gazz.* 27, II, 48). If the components are heated to a higher temperature without the condensing agent, stilbene is formed, carbon dioxide being split off (*von Walther*, *J. pr.* [2], 61, 171).  **$\alpha$ -Phenylcinnamic nitrile**, benzalbenzyl cyanide, m.p.  $86^\circ$ , obtained from benzyl cyanide, benzaldehyde, and sodium ethylate, gives the allo-form when irradiated with ultra-violet light. This form has b.p.  $213-214^\circ$  (23 mm.).  $\alpha$ -Phenylcinnamic acid gives  $\alpha$ -phenylhydrocinnamic acid on reduction, but does not add on bromine. By the action of bromine on the sodium salt, bromostilbene is formed (*Müller*, *Ber.* 26, 659).  **$\alpha$ -Phenyl-*o*-aminocinnamic acid**, m.p.  $186^\circ$ , the reduction product of  $\alpha$ -phenyl-*o*-nitrocinnamic acid, m.p.  $196^\circ$  (obtained by condensation of *o*-nitrobenzaldehyde and phenylacetic acid), gives 9-phenanthrene-carboxylic acid when its diazonium compound is shaken with copper powder (*Pschorr*, *Ber.* 29, 496; *Stoermer*, *Ann.* 409, 24). The  $\alpha$ -phenylcinnamic acid with m.p.  $172^\circ$ , and  $\alpha$ -phenyl-*o*-nitro- and *o*-aminocinnamic acids, of m.p.  $196^\circ$  and  $186^\circ$ , respectively, must have the *cis*-arrangement of the two phenyl groups. By irradiation with ultra-violet light,  $\alpha$ -phenyl-*o*-nitrocinnamic acid passes into allo- $\alpha$ -phenyl-*o*-nitrocinnamic acid, which melts at  $146-147^\circ$ . Allo-phenyl-*o*-aminocinnamic acid is not stable in the free state, but it gives a carbostyryl derivative (1); but its barium salt can be diazotised, which on boiling is smoothly converted into  $\alpha$ -phenyl-coumarin, m.p.  $140^\circ$  (2). By replacement of the amino-group in allo-phenyl-*o*-aminocinnamic acid with hydrogen, allo- $\alpha$ -phenylcinnamic acid, m.p.  $137^\circ$ , is formed. Thus the allo-series has a *trans*-arrangement of the phenyl groups (*Stoermer*, *Ann.* 409, 13):



$\alpha$ -Phenyl-coumarin is also obtained from salicylaldehyde and phenylacetic acid (*von Walther*, *J. pr.* [2], 61, 178). The nitrile of phenyl-*o*-aminocinnamic acid is readily transformed into  $\alpha$ -amino- $\beta$ -phenylquinoline, so that in syntheses, the latter is obtained instead of the nitrile (*Pschorr*, *Ber.* 32, 3399). *o*-, *m*-, and *p*-Hydroxybenzalbenzyl cyanide,  $\text{HO}C_6H_4CH:C(CN)C_6H_5$ , m.p.  $104^\circ$ ,  $107^\circ$  and  $192^\circ$  (*Borsche*, *Ber.* 37, 3163).

**$\alpha$ -Stilbene-methyl-ketone**, 3,4-diphenylbutenone-2,  $C_6H_5CH:C(C_6H_5)COCH_3$ , m.p.  $51^\circ$ , is obtained from benzaldehyde and phenylacetone by the action of hydrogen chloride gas. It does not add on bromine, but gives 3,4-diphenylbutanone-2,  $C_6H_5CH_2\cdot CH(C_6H_5)COCH_3$ , b.p.  $310^\circ$ , on reduction (*Goldschmidt*, *Mo.* 22, 659).

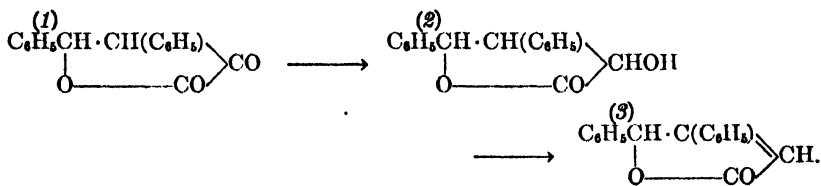
**Stilbene-propionic acid**,  $\gamma,\delta$ -diphenylallylacetic acid,  $C_6H_5CH:C(C_6H_5)\cdot CH_2CH_2COOH$ , m.p.  $106^\circ$ , is obtained by the action of benzaldehyde and acetic anhydride on sodium  $\alpha$ -phenylglutarate (*Fichter*, *Ber.* 34, 4177).

**Desylacetic acid**,  $\beta,\beta$ -phenylbenzoylpropionic acid,  $C_6H_5COCH(C_6H_5)CH_2COOH$ , m.p.  $161^\circ$ , is obtained in the form of its ester from sodio-desoxybenzoin and ethyl bromoacetate (*Thiele*, *Ann.* 319, 164). It is also obtained from the chloride of  $\beta$ -methyl hydrogen phenylsuccinate by the action of benzene and aluminium chloride (p. 435). When treated with acetic anhydride and sulphuric

acid in the cold the acid gives the *labile* diphenyl- $\Delta^2$ -crotonolactone,  $C_6H_5\overline{C}:C-(C_6H_5)CH_2COO$ , m.p.  $100^\circ$ , which, on boiling with acetic anhydride, or alkalis,

passes into the *stable* diphenyl- $\Delta^1$ -crotonolactone,  $C_6H_5\overline{CH}:C(C_6H_5):CHCOO$ , m.p.  $152^\circ$ . Both lactones give desylacetic acid when treated with alkali; the *stable* diphenyl-crotonolactone when acted upon by permanganate or bromine gives **desylene-acetic acid**,  $C_6H_5CO\cdot C(C_6H_5):CHCOOH$ , m.p.  $139^\circ$ . This compound can also be obtained from desylene-malonic ester, the condensation product of benzil and diethyl malonate (*Thiele*, *Ann.* 319, 155). Desylacetic acid and the *stable* diphenylcrotonolactone are also produced from  $\beta,\gamma$ -diphenyl- $\alpha$ -ketobutyro-lactone (1), the condensation product of phenylpyruvic acid and

benzaldehyde. This lactone gives a hydroxylactone (2) which, by loss of water gives diphenyl- $\Delta^1$ -crotonolactone (3), on reduction (Erlenmeyer, Ber. 31, 2218; Ann. 333, 160):



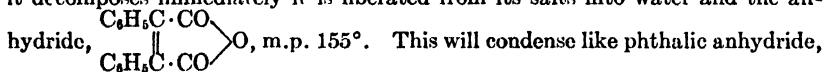
Dibenzyl-dicarboxylic acid, *sym*-diphenylsuccinic acid,  $\text{C}_6\text{H}_5\text{CHCOOH}$ , like  $\text{C}_6\text{H}_5\text{CHCOOH}$ ,

the *sym*-dialkylsuccinic acids, exists in two isomeric forms; the  $\alpha$ -acid (+2H<sub>2</sub>O) has m.p. 185° (anhydrous 220°), and is obtained by condensation of two mols. of phenylbromoacetic ester with potassium cyanide. By the action of sodium amalgam on stilbene dicarboxylic acid, both the  $\alpha$ - and  $\beta$ -acids are formed. The  $\beta$ -acid melts at 229°. The  $\alpha$ -acid is racemic, and can be resolved into its optical antipodes by means of the brucine salt. The  $\beta$ -acid is the meso-compound (Wren, J. 107, 144). With acetyl chloride, the  $\alpha$ -acid readily gives an anhydride, but the  $\beta$ -acid only with difficulty;  $\alpha$ -m.p. 116°,  $\beta$ -m.p. 112° (Poppe, Ber. 23, 117; Tillmanns, Ann. 258, 87; Anschütz, Ann. 259, 61). The nitrile,  $\text{C}_6\text{H}_5\text{CH}(\text{CN})\text{CH}(\text{CN})\text{C}_6\text{H}_5$ ,  $\alpha$ -m.p. 160°,  $\beta$ -m.p. 240°, is obtained by the condensation of phenylacetoneitrile with mandelonitrile by the action of potassium cyanide (Chalanay, Ber. 25, 289; Smith, Ber. 26, 60) and by the addition of hydrocyanic acid to  $\alpha$ -phenylcinnamoneitrile (Knoevenagel, Ber. 37, 4067). On hydrolysis both nitriles give the  $\beta$ -acid.

$\alpha, \beta$ -Diphenylglutaric acid,  $\text{C}_6\text{H}_5\text{CH}(\text{COOH})\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COOH}$ , m.p. 228°. The ester of this acid has been obtained by the addition of ethyl phenyl-acetate to ethyl cinnamate by means of sodium ethylate (Borsche, Ber. 42, 4497; Avery, Am. 30, 595). For the isomerism, preparation, and resolution of  $\alpha, \beta$ -diphenylglutaric acids, see Maclay, Am. 51, 2833.

$\beta, \gamma$ -Diphenyl-adipic acid,  $\text{COOHCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COOH}$ , exists in two forms, m.p. 270° and 170°, respectively. The dimethyl esters, m.p. 175° and 73°, respectively, are obtained by reduction of ethyl cinnamate with aluminium amalgam. Ethyl hydrocinnamate is a byproduct. The close similarity of this acid with truxillic acid should be noted (Henle, Ann. 348, 16; Jessen, Ber. 39, 4089). For the stereoisomerism of the two acids, and its connection with the truxic acids, see Oomen, J. 1930, 2148.

Stilbene-dicarboxylic acid, diphenylmaleic acid, is obtained as its ester by the action of sodamide on ethyl bromophenylacetate. Like the dialkyl maleic acids, it decomposes immediately it is liberated from its salts into water and the anhydride,



with phenylacetic acid, to give benzaldiphenyl-maleide,

$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{C} - \text{C} = \text{CHC}_6\text{H}_5 \\
 \parallel \quad \quad \diagdown \\
 \text{C}_6\text{H}_5\text{C} - \text{CO} \quad \text{O}
 \end{array}$$

which reacts in a similar way to benzalphthalide (p. 569) (Cohn, Ber. 24, 3854). The salts of diphenylmaleic acid are obtained by hydrolysis of the nitrile, dicyano-stilbene,  $\text{C}_6\text{H}_5\text{C}(\text{CN}) : \text{C}(\text{CN})\text{C}_6\text{H}_5$ , m.p. 158°, with alcoholic potash. Dicyano-stilbene is obtained by the action of potassium cyanide on phenyl-chloroacetoneitrile, or by the action of sodium ethoxide on it. It can also be obtained by the action of sodium ethoxide and iodine on phenylacetoneitrile (Chalanay, Ber. 25, 285; Michael, Ber. 25, 1680). Ethyl diphenyl maleate is converted into ethyl diphenylfumarate by the action of ultra-violet light. The free acid melts at 288-289° (Ramart-Lucas, Ann. chim. [10], 13, 385).

*o, o'*-Dicyanostilbene,  $\text{NCC}_6\text{H}_4\text{CH} : \text{CHC}_6\text{H}_4\text{CN}$ , m.p. 191.5-192.5°, is obtained from *o*-cyanobenzyl chloride through the *o*-cyanobenzyl-sulphonic acid (see Ruggli, Helv. 14, 541).

**Stilbene-succinic acid**,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{C}_6\text{H}_5)\text{CH} \begin{matrix} \text{COOH} \\ \text{CH}_2\text{COOH} \end{matrix}$ , is obtained by the condensation of desoxybenzoin (p. 562) with ethyl succinate by means of sodium ethylate. With bromine the acid gives a bromolactonic acid, which on heating gives an unsaturated lactonic acid,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{C}_6\text{H}_5):\text{C}(\text{COO})\text{CH}_2\text{COOH}$ , and a dilactone,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{C}_6\text{H}_5):\text{CH}(\text{COO})\text{CH}_2\text{COO}$  (*Russwurm*, Ann. 308, 156).

A derivative of dibenzyl is 4,5-diphenyloctane-2,7-dione, or  $\alpha,\beta$ -diacetyl-dibenzyl,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_2\text{COCH}_3)_2$ , m.p.  $161^\circ$ , b.p.  $335\text{--}340^\circ$ , which is produced in the reduction of 2 mols. of benzylidene-acetone in weakly acid or neutral solution. Homologous diketones are produced by the reduction of homologous benzylidene-ketones (*Harries*, Ber. 29, 380, 2121).

### (c) tri-, tetra-, penta-, and hexa-Phenylethane Group

**Triphenylethane**,  $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{C}_6\text{H}_5$ , b.p.  $318^\circ$ , (*Klages*, Ber. 37, 1455) is obtained by reducing triphenylethylene.

**Triphenylethylene**,  $\alpha$ -phenylstilbene,  $(\text{C}_6\text{H}_5)_2\text{C}:\text{CHC}_6\text{H}_5$ , m.p.  $68^\circ$ , b.p.  $221^\circ$  (14 mm.), is formed by the removal of water from benzyl-diphenylcarbinol,  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ , m.p.  $89^\circ$ , which is itself obtained by the action of benzyl magnesium chloride on benzophenone, or by the action of phenyl magnesium bromide on desoxybenzoin, or ethyl phenylacetate (*Hell*, Ber. 37, 1429; *Klages*, Ber. 37, 1455).  $\alpha$ -Triphenylacetaldehyde, m.p.  $105.5^\circ$ , is obtained by the action of concentrated sulphuric acid on triphenylethanone.

**Triphenylethanone**,  $(\text{C}_6\text{H}_5)_2\text{CHCOC}_6\text{H}_5$ , m.p.  $136^\circ$ , is obtained by the action of benzene and aluminium chloride on chloral, dichloro- or trichloro-acetyl chloride, desyl chloride, or acetylmandelyl chloride (*Collet*, Bull. [3], 15, 22; *Biltz*, Ann. 296, 219; *Anschütz*, Ann. 368, 92). It can also be obtained by warming triphenylethylene glycol with 25% sulphuric acid (*Triffeneau*, C.r. 146, 29; *Orekhoff*, Bull. [4], 25, 186). **Triphenylethylene glycol**,  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}(\text{OH})\text{C}_6\text{H}_5$ , m.p.  $164^\circ$ , is obtained by the action of phenyl magnesium bromide on benzoin or ethyl mandelate (*Acree*, Ber. 37, 2762). Triphenylethanone is decomposed by permanganate into benzophenone and benzoic acid, and by alcoholic potash into diphenylmethane and benzoic acid. It gives an oxime, m.p.  $182^\circ$ , with hydroxylamine hydrochloride (*Kohler*, Am. 36, 177). With acetyl chloride and benzoyl chloride, on the other hand, triphenylvinyl acetate and benzoate, respectively, are formed. These are derivatives of the enol form. According to optical measurements, pure triphenylethanone is the ketoform (*Ley*, Ber. 56, 777). With bromine in carbon disulphide it gives triphenyl-bromoethanone,  $(\text{C}_6\text{H}_5)_2\text{CBrCOC}_6\text{H}_5$ , m.p.  $97^\circ$ , but in glacial acetic acid, bromine is replaced by OH and triphenyl-hydroxyethanone, or phenylbenzoin,  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{COC}_6\text{H}_5$ , m.p.  $84^\circ$ , is formed. This substance is also obtained by the oxidation of triphenyl-ethanone with nitric acid, and by the action of phenyl magnesium bromide on benzil (*Biltz*, Ber. 32, 650; *Acree*, Ber. 37, 2758). **Triphenylethanol**,  $(\text{C}_6\text{H}_5)_2\text{C}\cdot\text{CH}_2\text{OH}$ , m.p.  $110.5^\circ$ , is obtained by reduction of triphenylacetaldehyde or triphenyl-ethanone (*Gardeur*, Bull. acad. roy. Belg. [3], 34, No. 7, 67).

**Triphenylmethylethane**,  $\alpha,\alpha,\beta$ -triphenylpropane,  $(\text{C}_6\text{H}_5)_2\text{CHCH}(\text{CH}_3)\text{C}_6\text{H}_5$ , is probably obtained in the reduction of diphenylindone with phosphorus and hydriodic acid.

$\alpha,\beta,\beta$ -Triphenylpropane. The hydroxy-derivatives of this hydrocarbon have been prepared by the action of chloroacetone on phenols. Trihydroxy derivative, m.p.  $175^\circ$ , hexahydroxy-derivative, m.p.  $180^\circ$  (*Lippmann*, Ber. 45, 2489).

**Ethyl triphenylacrylate**,  $(\text{C}_6\text{H}_5)_2\text{C}:\text{C}(\text{C}_6\text{H}_5)\text{COOR}$ , is obtained by the condensation of benzophenone chloride with ethyl phenylacetate. The corresponding acid, m.p.  $213^\circ$ , has been obtained from  $\alpha,\beta,\beta$ -triphenylpropionic acid, by bromination and splitting off HBr, and from the nitrile, m.p.  $163^\circ$ , obtained by the condensation of diphenyl-dichloromethane and benzyl cyanide (*Heyl*, Ber. 28, 2784;

*Dahl*, Ber. 29, 2841; cf. *Stobbe*, Ber. 34, 1963).  $\alpha, \beta$ -Triphenylpropionic acid,  $(C_6H_5)_3CH \cdot CH(C_6H_5)COOH$ , m.p.  $211^\circ$ , is obtained by the action of phenyl magnesium bromide on  $\alpha$ -phenylcinnamic ester. When diphenylindone is fused with alkalis, an acid isomeric with triphenylacrylic acid is obtained. It melts at  $186^\circ$ , and is apparently  $\alpha, \beta$ -diphenylvinyl- $\alpha$ -benzoic acid,  $COOH[1]C_6H_4[2]C(C_6H_5):CHC_6H_5$ . Both acids are converted into diphenylindone when heated with zinc chloride.

$\alpha, \alpha, \beta$ -Triphenylpropionic acid,  $C_6H_5 \cdot CH_2 \cdot C(C_6H_5)_2 \cdot COOH$ , m.p.  $132^\circ$ , is obtained by the action of benzyl chloride on sodio-diphenylacetobenzyl ester, followed by hydrolysis. The nitrile melts at  $126^\circ$  (*Ramart*, C.r. 178, 93).

$\beta, \beta$ -Triphenylpropionic acid, m.p.  $178-179^\circ$  (*Gagnon*, Ann. chim. [10] 12, 296).

*sym*-Tetraphenylethane,  $(C_6H_5)_2CH \cdot CH(C_6H_5)_2$ , m.p.  $209^\circ$ , b.p.  $379-383^\circ$ , is obtained by heating benzophenone, or diphenylchloro- or -bromomethane with zinc, colloidal silver, or sodium in benzene solution, and by the action of copper on thiobenzophenone. It can also be obtained by the reduction of tetraphenylethylene with sodium and alcohol, by the action of hydriodic acid and phosphorus on benzpinacolone or benzpinacolone, and by condensation of stilbene bromide, tetrabromoethane or chloral with benzene and aluminium chloride (*Anschütz*, Ber. 18, 657; *Biltz*, Ber. 26, 1952; Ann. 296, 221).

*as*-Tetraphenylethane,  $(C_6H_5)_3C \cdot CH_2C_6H_5$ , m.p.  $144^\circ$ , is obtained by the action of benzyl magnesium chloride on triphenyl-chloromethane, or of triphenyl-methyl magnesium chloride, or potassium-triphenylmethyl on benzyl chloride (*Schmidlin*, Ber. 41, 435).

Tetraphenylethylene,  $(C_6H_5)_2C:C(C_6H_5)_2$ , m.p.  $221^\circ$ , is obtained, together with tetraphenylethane, by the action of zinc on benzophenone. It is also obtained, together with the benzpinacolines by heating diphenyl-dichloromethane with silver or zinc dust (*Lohse*, Ber. 29, 1789), and by heating diphenyl-chloromethane with diphenylmethane (*Norris*, Ber. 43, 2958). When oxidised it is decomposed into two molecules of benzophenone. In carbon tetrachloride solution it combines with chlorine to give tetraphenylethylene dichloride,  $(C_6H_5)_2CCl \cdot CCl(C_6H_5)_2$ , m.p.  $186^\circ$ , which can also be obtained from diphenyl-dichloromethane by the action of colloidal silver or mercury, or sodium iodide in acetone solution. Bromine and iodine do not add on to tetraphenylethylene. It gives crystalline addition products with two molecules of chloroform or carbon tetrachloride. The two chlorine atoms in tetraphenylethylene dichloride are very loosely bound. On heating it breaks down into tetraphenylethylene and chlorine, and the chlorine partially substitutes. On boiling with water  $\alpha$ -benzpinacolone is formed; and with methyl alcohol,  $\beta$ -benzpinacolone is obtained. By the action of aluminium chloride on the benzene solution two molecules of HCl are split off and 9,10-diphenyl-phenanthrene is formed. (*Finkelstein*, Ber. 43, 1533; *Norris*, Ber. 43, 2940).

Tetramethyl-diamino-tetraphenylethylene,  $(CH_3)_2NC_6H_4(C_6H_5)C:C(C_6H_5)-C_6H_4N(CH_3)_2$ , m.p.  $225^\circ$ , is obtained by the reduction of dimethylamino-benzophenone with tin and hydrochloric acid. It gives an intense red colour when acted upon by oxidising agents, such as ferric chloride in acid solution (*Willstätter*, Ber. 39, 3765), which is ascribed to the formation of carbonium salts of tetraphenylethylene. The tendency towards the formation of these tetraphenylethane dyes is shown particularly in the addition of the halogens with the formation of compound of the type  $[(R \cdot C_6H_4)_2-C^+-C^+-(C_6H_4 \cdot R)_2]^{++}2X^-$ . These dyes have been prepared from tetrahydroxy-tetraphenylethylene as well as from tetramethyl-diamino-tetraphenylethylene (*Wizinger*, Ber. 60, 1377; *Madelang*, Ber. 60, 2469).

**ALCOHOLS OF THE TETRAPHENYLETHANE GROUP:** In addition to tetraphenyl-ethanol,  $(C_6H_5)_2CH-C(OH)(C_6H_5)_2$ , m.p.  $235-236^\circ$ , which can be obtained from triphenyl-ethanone and phenyl magnesium bromide (*Orekhoff*, Bull. [4], 25, 186), the pinacones of benzophenone and its homologues must be mentioned. Like the pinacones of the aliphatic series, these compounds are obtained from the ketones by the action of nascent hydrogen, secondary alcohols being formed at the same time.

Benzpinacolone, or tetraphenylethylene glycol,  $(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$ , m.p.  $187^\circ$ , decomposes on melting into benzophenone and diphenylcarbinol. The same fission is brought about by boiling the substance with alcoholic potash.

It is obtained from benzophenone by the action of zinc and sulphuric acid, and by the decomposition of sodio-benzophenone (*Beckmann*, *Ann.* 266, 1), or by condensation of methyl oxalate or ethyl benzilate with phenyl magnesium bromide (*Valeur*, *C.r.* 136, 94; *Acree*, *Ber.* 37, 2761). On warming with concentrated hydrochloric acid or dilute sulphuric acid to 200°, benzpinacone, like the ordinary pinacones, loses water, and a migration of the phenyl group takes place, giving  $\beta$ -benzpinacolone,  $(C_6H_5)_3C \cdot COC_6H_5$ , m.p. 179°. This compound can be obtained synthetically by the action of triphenylmethyl magnesium chloride on benzaldehyde and subsequent oxidation, and by the action of phenyl magnesium bromide on triphenylacetyl chloride (*Schmidlin*, *Ber.* 43, 1140). Its constitution is arrived at from these two syntheses, and from its fission into triphenylmethane and benzoic acid when heated with soda-lime and by the formation of triphenylcarbinol and benzoic acid on oxidation.  $\beta$ -Benzpinacolone can also be obtained directly from benzophenone by the action of zinc dust and acetyl chloride, the isomeric  $\alpha$ -benzpinacolone, m.p. 203°, being formed at the same time.  $\alpha$ -Benzpinacolone is readily converted into the  $\beta$ -compound by acids, and is to be con-

sidered as tetraphenyl-ethylene oxide,  $(C_6H_5)_2C \cdot O \cdot C(C_6H_5)_2$  (*Klinger*, *Ber.* 29, 2158; *Schmidlin*, *Ber.* 43, 1153). When heated with zinc ethyl  $\beta$ -benzpinacolone is converted into benzpinacolone alcohol,  $(C_6H_5)_3C \cdot CH(OH)C_6H_5$ , m.p. 151°. When this compound is heated with acetic anhydride, the phenyl group migrates back, and tetraphenylethylene is formed (*Delacre*, *Bull.* [3], 4, 470). (Cf. the analogous behavior of pinacolone alcohol, when tetramethyl-ethylene is formed, Vol. I). For  $p,p',p'',p'''$ -tetrachloro-benzpinacolone, see *Montagne*, *Rec.* 25, 379. Tetraphenyl-ethylene sulphide,  $(C_6H_5)_2C \text{---} S \text{---} C(C_6H_5)_2$ , decomp. at 175°, is the

sulphur compound corresponding to  $\alpha$ -benzpinacolone, and is obtained by the action of diazomethane on thiobenzophenone. On heating, sulphur is split off, and tetraphenylethylene formed (*Staudinger*, *Helv.* 3, 833).

Pentaphenylethane,  $(C_6H_5)_3C \cdot CH(C_6H_5)_2$ , m.p. 179° in an atmosphere of carbon dioxide, is obtained by the action of diphenylmethyl magnesium bromide,  $(C_6H_5)_2CHMgBr$ , on triphenylchloromethane (*Gomberg*, *Ber.* 39, 1466), and by the action of zinc on a mixture of diphenylbromomethane and triphenylchloromethane in ethyl acetate (*Norris*, *Ber.* 43, 2945). It is not so stable as tetraphenylethane, and in this respect it resembles hexaphenylethane, which readily dissociates. On heating in the air it takes up oxygen and decomposes. When its solution in anisole or ethyl benzoate is boiled it breaks down into triphenylmethyl, or hexaphenylethane, and *sym*-tetraphenylethane (*Schlenk*, *Ber.* 43, 3541) (cf. Vol. IV):



It decomposes in a similar way when heated with HCl in benzene, or when acted upon with sulphuryl chloride (*Tshitshibabin*, *Ber.* 40, 367; *Norris*, *Ber.* 43, 2945).

Pentaphenylethyl alcohol,  $(C_6H_5)_3C \cdot C(OH)(C_6H_5)_2$ , m.p. 179°, is obtained from  $\beta$ -benzpinacolone and phenyl magnesium bromide (*Schmidlin*, *Ber.* 43, 1145).

Hexaphenylethane,  $(C_6H_5)_3C \cdot C(C_6H_5)_3$ , m.p. 145–147°. This exceedingly interesting hydrocarbon was first obtained by *Gomberg* in 1900 (*Ber.* 33, 3150) by the action of zinc on a benzene solution of triphenylchloromethane (for preparation, see *Schlenk*, *Ann.* 372, 17). It is characterised by its great reactivity, which is due to the fact that in solution, hexaphenylethane is partly dissociated into the free radical triphenylmethyl:



For this radical and its reactions, see Vol. IV.

In addition to the methods already given, hexaphenyl-ethane can be obtained by the following reactions: 1. by the action of triphenylmethyl magnesium chloride on triphenylchloromethane (*Schmidlin*, *Ber.* 41, 423); 2. by the electrolysis of triphenylbromomethane in liquid sulphur dioxide (*Schlenk*, *Ann.* 372, 11); 3. from hydrazotriphenylmethane,  $(C_6H_5)_3C \cdot NH \cdot NH \cdot C(C_6H_5)_3$ , by oxidation with potassium hypobromite. The unstable azo-compound is formed immediately (*Wiand*, *Ber.* 42, 3020).



**Tetraphenylethane-dicarboxylic acid, tetraphenyl-succinic acid,**  
 $(C_6H_5)_2CCOOH$

$(C_6H_5)_2CCOOH$ , m.p. 261° (decomp.) (ethyl ester m.p. 89°), is obtained by the action of silver on ethyl diphenylchloroacetate (*Bickel*, Ber. 22, 1538). Its nitrile, m.p. 215–220°, is obtained by the action of sodium and iodine on diphenylacetone nitrile. For another method of preparing tetraphenylsuccinic acid, see *Stollé*, Ber. 45, 3113).

The dilactone of a benzpinacene-*o,o'*-dicarboxylic acid,  $\overline{O}OCC_6H_4C(C_6H_5)_2C(C_6H_5)_2COO$ , m.p. 265°, is obtained by boiling *o*-benzoylbenzoic acid (p. 522), with hydriodic acid and phosphorus (*Ullmann*, Ann. 291, 17).

#### (d) $\omega,\omega$ -Diphenylpropane Group

**Dibenzylmethane,  $\alpha,\gamma$ -diphenylpropane,**  $C_6H_5CH_2 \cdot CH_2 \cdot CH_2C_6H_5$ , b.p. 290–300°, m.p. 15–16°, is obtained by the reduction of dibenzyl-ketone (see below) with hydriodic acid, from benzal-acetophenone with a nickel catalyst, in which case dicyclohexylpropane is also formed, or by the action of caustic potash on phenylacetaldehyde (*Stoermer*, Ber. 58, 2697).

**$\alpha,\gamma$ -Diphenylpropylene,**  $C_6H_5CH_2 \cdot CH : CHC_6H_5$ , b.p. 179° (15 mm.), is an oil smelling like hyacinth, obtained from  $\alpha,\gamma$ -diphenylpropyl alcohol, b.p. 193° (12 mm.), by the action of anhydrous oxalic acid. It can also be obtained from  $\beta$ -bromodibenzylacetic acid by warming with dilute caustic soda (*Dieckmann*, Ber. 39, 3046).

**$\alpha,\beta,\gamma$ -Triphenylpropane,** b.p. 225–230° (10 mm.). When desoxybenzoin is treated with benzyl magnesium bromide,  $\alpha,\beta,\gamma$ -triphenylpropanol-(2), m.p. 86–87°, is formed, and this, when treated with phosphorus and hydriodic acid gives triphenylpropane (*Fuson*, Am. 48, 2937).

**$\alpha,\beta,\gamma$ -Triphenylpropene,** m.p. 63–64°, is obtained by removal of water from triphenylpropanol (see above). When its dibromide is boiled with glacial acetic acid it gives 2,3-diphenylindene (p. 593) (*Orichoff*, Ber. 47, 89; *Ramart*, C.r. 182, 1342).

**$\alpha,\alpha,\gamma$ -Triphenylpropanol-(1),** see *Ramart*, C.r. 182, 1342.

**$\alpha,\alpha,\gamma$ -Triphenylhydroxy-(1)-propene-(2),** m.p. 95°,  $(C_6H_5)_2C(OH)CH : CH(C_6H_5)$ , is obtained from benzophenone and the magnesium compound of  $\beta$ -bromostyrene. With acetic anhydride it is converted into triphenylallene,  $(C_6H_5)_2C : C : CH(C_6H_5)$  (*Straus*, Ann. 442, 93).

**Tetraphenylallene,**  $(C_6H_5)_2C : C : C(C_6H_5)_2$ , m.p. 164°, is obtained by the dry distillation of barium diphenylacetate (*Vorländer*, Ber. 39, 1024) or from  $\alpha,\alpha,\gamma,\gamma$ -tetraphenyl- $\beta$ -propylene alcohol and acetic anhydride (*Vorländer*, Ber. 56, 1136). It readily polymerises to 1,3-diphenyl-hydrindene (*Krause*, Ber. 57, 534), and on reduction with hydriodic acid it gives tetraphenylpropylene, m.p. 127–128°, and tetraphenylpropane (*Vorländer*, Ber. 56, 1122). For substituted tetraphenylallenes, see *Bergmann*, J. pr. [2], 135, 245.

**Dibenzyl-ketone,**  $C_6H_5CH_2 \cdot CO \cdot CH_2C_6H_5$ , m.p. 40°, b.p. 330°, is obtained by the distillation of calcium or barium phenylacetate (*Apitzsch*, Ber. 37, 1428). In the two  $CH_2$  groups of this ketone, one H atom is readily replaced by sodium, and hence by an alkyl group (*Opolski*, Bull. Acad. Sci. de Cracovie, 1900). It condenses with ethyl oxalate and sodium ethylate to give a triketocyclopentane derivative, oxalyl-benzyl-ketone (cf. Vol. II). With benzylidene-aniline it gives an addition product which occurs in various forms (*Francis*, J. 75, 865). With phosphorus pentachloride it gives 1,3-diphenyl-2-chloropropylene,  $C_6H_5CH_2 \cdot CCl : CHC_6H_5$ , b.p. 181° (12 mm.), and with nitrous acid, diisonitroso-dibenzyl-ketone,  $C_6H_5C(NO) \cdot COC(NO)C_6H_5$ , m.p. 133° (*Vorländer*, Ber. 37, 1134). On reduction with sodium, dibenzyl-ketone gives dibenzyl carbinol,  $(C_6H_5CH_2)_2 \cdot CHOH$ , b.p. 327°. It condenses with phenol to give dibenzyl-diphenol-methane,  $(C_6H_5CH_2)_2C(C_6H_4OH)_2$  (*Bogdanovska*, Ber. 25, 1271). **Dibenzyl-phenyl carbinol,**  $(C_6H_5CH_2)_2C(OH)C_6H_5$ , m.p. 87°, and **tribenzyl-carbinol,**  $(C_6H_5CH_2)_3 \cdot C(OH)$ , m.p. 115°, are obtained from ethyl benzoate and ethyl phenylacetate with two molecules of benzyl magnesium chloride (*Klages*, Ber. 37, 1456).

**Benzyl-acetophenone,**  $C_6H_5CH_2 \cdot CH_2COC_6H_5$ , m.p. 73°, is isomeric with dibenzyl-ketone. It is obtained by reduction of

**Benzylidene-acetophenone**, or chalkone (*Kostanecki*, Ber. 32, 1923),  $C_6H_5CH:CHCO \cdot C_6H_5$ , m.p. 58°, b.p. 346°, with zinc dust and acetic acid. Chalkone is obtained by the condensation of benzaldehyde and acetophenone with sodium methylate. It gives two stereoisomeric oximes, m.p. 75°, and 116°, the latter giving cinnamic anilide when subjected to the Beckmann transformation (*Henrich*, Ann. 351, 172). It combines with hydrochloric acid giving **chlorobenzylacetophenone**,  $C_6H_5CHClCH_2CO \cdot C_6H_5$ , and with bromine to give a dibromide,  $C_6H_5CHBr \cdot CHBr \cdot CO \cdot C_6H_5$ , m.p. 158°, which gives dibenzoyl-methane with alcoholic potash, and with potassium acetate monobromo-benzylidene-acetophenone,  $C_6H_5 \cdot CBr:CHCO \cdot C_6H_5$ , m.p. 44°. A second dibromide of chalkone, m.p. 122-123°, is readily obtained by the action of hydrogen bromide on  $\alpha$ -bromobenzyl-acetophenone (*Abell*, J. 101, 998). This compound is also obtained as a by-product in the direct bromination of chalkone. By the action of nitrous fumes on chalkone, various products are obtained, among which the dinitrite,  $(C_{10}H_{12}O)N_2O_4$ , may be mentioned. This compound gives **benzal-nitro-acetophenone**,  $C_6H_5CH:C(NO_2)CO \cdot C_6H_5$ , with dilute caustic soda, and when this is reduced with tin and hydrochloric acid in methyl alcohol, **benzylisonitroso-acetophenone**,  $C_6H_5CH_2 \cdot C(OH) \cdot CO \cdot C_6H_5$ , m.p. 126° is formed. This is an oxime of diphenyl-diketopropane, isomeric with dibenzoylmethane (*Wieland*, Ber. 36, 3015; Ann. 340, 63).

For absorption determinations with the chalkones, see *Shibata*, Acta phytochim. 2, 25. For the halochromism of chalkone and its derivatives, see J. pr. [2], 124, 81.

Many derivatives of chalkone are characterised by the ability to exist in many polymorphic forms, e.g., three forms of *p*'-methyl-chalkone,  $C_6H_5 \cdot CH:CH \cdot CO \cdot C_6H_4 \cdot CH_3$ , are known, melting at 77° ( $\alpha$ ), 59° ( $\beta$ ), and 45° ( $\gamma$ ), respectively. They are obtained by condensation of benzaldehyde with *p*-methyl-acetophenone. The  $\alpha$ -form is the most stable, the  $\beta$ -form may be retained for a year in the absence of the  $\alpha$ -form, and the  $\gamma$ -form has a life-period of only a few days. All the forms are mutually convertible (*Weygand*, Ann. 449, 29).

**Hydrochalkone**,  $C_6H_5 \cdot (CH_2) \cdot CO \cdot C_6H_5$ , m.p. 72°, is obtained by the catalytic reduction of chalkone. When treated with sodium amalgam in alcohol it is reduced to hydrochalkol, b.p. (13 mm.) 188-191°. This compound splits off water forming diphenyl-propene (*Nekrassov*, J. pr. [2], 119, 109).

*p,p'*-**Dichlorobenzylidene-acetophenone**, m.p. 157°, gives a "keto-chloride,"  $ClC_6H_4 \cdot CCl:CH \cdot CHCl \cdot C_6H_4Cl$ , m.p. 55°, when acted upon by phosphorus pentachloride in benzene solution. In this reaction there has not been a simple substitution of carbonyl oxygen by halogen, but a transformation, arising from the mobility of the chlorine atom. The chlorine atom attached to the saturated C atom is readily replaceable by hydroxyl or methoxyl (*Straus*, Ann. 393, 249). These compounds dissolve in concentrated sulphuric acid with an intense colouration (*Straus*, Ber. 42, 1804) (*cf.* also dibenzylidene-acetone, p. 587).

*o*-, *m*-, and *p*-**Hydroxybenzylidene-acetophenone**,  $HOC_6H_4CH:CHCO \cdot C_6H_5$ , m.p. 154° (decomp.), 160°, and 183°, respectively, are obtained by the action of acetophenone on the corresponding hydroxybenzaldehydes, or by the Friedel-Crafts reaction using cinnamyl chlorides and phenolic ethers (*Stockhausen*, Ber. 25, 3536). The isomeric **benzylidene-*o*-, *m*-, and *p*-hydroxy-acetophenones**, m.p. 89°, 126° and 173°, respectively, are obtained from benzaldehyde and the hydroxy-acetophenones. For the colour of the isomers, see *Kostanecki*, Ber. 32, 1921. A number of polyhydroxybenzylidene-acetophenones are found in nature in the form of their glucosides. **Butein**,  $(HO)_2[3,4]C_6H_2CH:CHCO \cdot C_6H_2[2',4']-(OH)_2$ , forming orange-yellow needles, m.p. 214°, occurs as a glucoside in the flowers of *Butea frondosa*. It decomposes when boiled with caustic potash into protocatechuic acid and resacetophenone (*Perkin*, Proc. 20, 169). It has been synthesised from protocatechuic aldehyde and resacetophenone, or from dicarboxy-caffeic chloride and resorcinol. When treated with hydrochloric acid it is converted into **butin** (7,3',4'-trihydroxyflavanone) (*Shinoda*, J. pharm. soc. Japan, 49, 123). **Naringenin**,  $HO[4]C_6H_4CH:CH \cdot CO \cdot C_6H_2[2',4',6']-(OH)_2$ , m.p. 248°, and **hesperitin**,  $HO[3](CH_3O)[4]C_6H_2CH:CH \cdot CO \cdot C_6H_2[2',4',6']-(OH)_2$ , m.p. 224°, are obtained by the hydrolysis of the glucosides naringin, and hesperidin, respectively (Vol. II, p. 360) with dilute acid. For synthesis, see *Shinoda, loc. cit.*). When boiled with caustic potash they give phloroglucinol and *p*-cumaric acid, and isoferulic acid, respectively. **Sakuranetin** is the 7-mono-

methyl ether of naringenin. **Homoeiriodictyol**,  $\text{HO}[4](\text{CH}_3\text{O})[3]\text{C}_6\text{H}_4\text{CH}:\text{CH}\cdot\text{COC}_6\text{H}_5[2',4',6'](\text{OH})_3$ , m.p.  $223^\circ$ , is isomeric with hesperitin. It has been isolated, together with **eriodictyol**,  $(\text{HO})_3[3,4]\text{C}_6\text{H}_4\text{CH}:\text{CHCOC}_6\text{H}_5[2',4',6'](\text{OH})_3$ , m.p.  $267^\circ$ , from the leaves of *Eriodictyon californicum* (Tutin, J. 97, 2054). **Phloretin** occurs as the glucoside phloridzin, in the bark of apple and pear trees. It is a tetrahydroxy derivative of chalcone,  $\text{HO}[4]\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5[2',4',6'](\text{OH})_3$ . The sugar radical is attached in the 2-position (Wessely, Mo. 53/54, 554). For its synthesis, see *Shinoda, loc. cit.*; *Fischer*, Ber. 50, 611. When benzylidene-*o*-hydroxyacetophenone is boiled with mineral acids, it is converted into the isomeric **flavanone**,  $\text{C}_6\text{H}_5\begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{CH} \diagup \\ \diagup \text{CO} \diagdown \\ \diagdown \text{CH}_2 \diagup \end{array} \text{C}_6\text{H}_5$ , a reaction which has

been used to discover the constitution of many of the vegetable dyes belonging to this group, such as quercetin, fisetin, luteolin, etc. The dibromide of acetyl-*o*-hydroxybenzylidene-acetophenone gives **benzoyl-coumarone**,

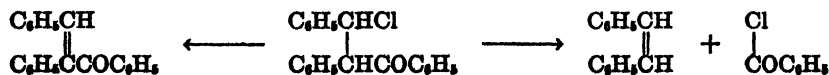
$\text{C}_6\text{H}_5\begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{CH} \diagup \\ \diagup \text{CCOC}_6\text{H}_5 \diagdown \end{array}$ , when treated with alcoholic potash. *o*-Hydroxybenzylidene-acetophenone gives  $\alpha$ -phenyl- $\gamma$ -(*o*-hydroxyphenyl)-propyl alcohol,  $\text{HOC}_6\text{H}_4\cdot\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{C}_6\text{H}_5$ , m.p.  $97^\circ$ , when reduced. This compound forms a cyclic ether,  $\text{C}_6\text{H}_5\begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \\ \diagup \text{CH}_2 \diagdown \\ \diagdown \text{CHC}_6\text{H}_5 \diagup \end{array}$ , with methyl alcoholic HCl (*Kostanecki*, Ber. 29, 244; *Harries*, Ber. 29, 375).

**Diphenyl-styryl carbinol**,  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_5$ , m.p.  $110.5^\circ$ , is obtained by the action of styryl magnesium bromide on benzophenone (*K. H. Meyer*, Ber. 55, 815). When methylated with methyl alcohol and acid, it undergoes transformation into the methyl ether of 1,3,3-triphenyl-allyl alcohol,  $(\text{C}_6\text{H}_5)_2\text{C}:\text{CH}-\text{CH}(\text{OCH}_3)\text{C}_6\text{H}_5$ , m.p.  $97-98^\circ$ . The normal ether of diphenyl-styryl carbinol, m.p.  $79^\circ$ , is obtained from 1,1,3-triphenyl-propene(1) through the dibromide, replacement of the two adjacent bromine atoms in the two phenyl nuclei by methoxy, and splitting off HBr (*Ziegler*, Ann. 443, 161).

*o*-Hydroxy-styryl-diphenyl carbinol,  $\text{HO}[2]\text{C}_6\text{H}_4\text{CH}:\text{CHC}(\text{OH})(\text{C}_6\text{H}_5)_2$ , m.p.  $164-166^\circ$ , is obtained from coumarin and two mols. of phenyl magnesium bromide (*Kohler*, Am. 29, 352; *Houben*, Ber. 37, 496).

Two molecules of acetophenone will condense spontaneously on heating, or when warmed with zinc ethyl or zinc chloride to give a homologue of benzal-acetophenone called **dypnone**,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3):\text{CHCOC}_6\text{H}_5$ , b.p.  $225^\circ$  (22 mm.). This compound is related to acetophenone in the same way as mesityl oxide is to acetone (*Delacre*, Belg. [3], 26, 534). When heated dypnone decomposes into an unsaturated hydrocarbon, diphenylfuran and triphenylbenzene (p. 508) (*Ameys*, Belg. 1899, 227). Dypnone combines with hydroxylamine when allowed to stand with it in alcoholic solution, forming **dypnone-hydroxylamine**,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{CH}_3)(\text{NHOH})\cdot\text{CH}_2\text{COC}_6\text{H}_5$ , m.p.  $110^\circ$ . Under other conditions, two **dypnone oximes**,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3):\text{CHC}(\text{NOH})\text{C}_6\text{H}_5$ , m.p.  $78^\circ$  and  $134^\circ$ , respectively, are formed. The second of these gives the anilide of  $\beta$ -methyl-cinnamic acid (p. 569) when submitted to the Beckmann transformation (*Binz*, Ber. 37, 730).

Benzaldehyde condenses with desoxybenzoin just as easily as acetophenone does. Under the influence of alkalis **benzylidene-desoxybenzoin**,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{C}_6\text{H}_5)\text{COC}_6\text{H}_5$ , m.p.  $101^\circ$ , is formed. This is also obtained, together with **isobenzylidene-desoxybenzoin**, m.p.  $89^\circ$ , by distillation of benzamarone (p. 588). The iso-compound is easily converted into the higher melting isomeride, and is also formed by condensation of benzaldehyde and desoxybenzoin with hydrochloric acid. In this case **chlorobenzyl-desoxybenzoin**, m.p.  $172^\circ$ , is formed at the same time, a compound which is readily converted by alkalis into the benzylidene-desoxybenzoin melting at  $101^\circ$ . On distillation, however, it breaks down into stilbene and benzoyl chloride (*Klages*, Ber. 26, 447; *Klingemann*, Ber. 26, 818; *Stobbe*, Ber. 34, 3897; *Klages*, Ber. 35, 3965):



Benzylidene-desoxybenzoin gives **benzyl-desoxybenzoin**,  $C_6H_5CH_2CH(C_6H_5)-COC_6H_5$ , m.p.  $120^\circ$ , on reduction. This compound is obtained directly by the benzoylation of desoxybenzoin. With acetic anhydride, glacial acetic acid, and concentrated sulphuric acid it gives a derivative of 2,3-diphenylindene (*Thiele*, *Ann.* 393, 61).

$\beta,\beta$ -Diphenylpropiofenone,  $C_6H_5COCH_2\cdot CH(C_6H_5)_2$ , m.p.  $96^\circ$ , is obtained by the addition of 1 molecule of phenyl magnesium bromide to benzylidene-acetophenone (*Kohler*, *Am.* 31, 642).

$\alpha,\beta,\beta$ -Triphenylpropiofenone,  $C_6H_5COCH(C_6H_5)CH(C_6H_5)_2$ , m.p.  $182^\circ$ , is obtained in a similar way from phenyl magnesium bromide and benzylidene-desoxybenzoin in ether solution, and by the action of an excess of phenyl magnesium bromide on ethyl  $\alpha$ -phenyl-cinnamate. In ligroin solution it is possible to isolate as the first addition product **tetraphenyl-propenol**,  $C_6H_5C(OH):C(C_6H_5)CH(C_6H_5)_2$ . This melts at  $95-100^\circ$ , and is transformed into triphenyl-propiofenone. It rapidly absorbs oxygen forming a peroxide melting at  $127^\circ$ , which on heating breaks down into diphenylacetophenone and benzoic acid (*Kohler*, *Am.* 36, 177).

**Tetraphenyl-acetone**,  $(C_6H_5)_2CH\cdot CO\cdot CH(C_6H_5)_2$ , m.p.  $134-135^\circ$ , is obtained by the action of sodium on ethyl diphenyl-acetate.

**Benzoyldibenzyl-methane**, dibenzyl-acetophenone,  $C_6H_5COCH(CH_2C_6H_5)_2$ , m.p.  $78^\circ$ , is obtained by heating acetophenone with benzyl chloride and caustic soda to  $160-170^\circ$  (*Nef*, *Ann.* 310, 322).

**Phenacyl-phthalide**,  $C_6H_5\begin{matrix} \diagup CHCH_2COC_6H_5 \\ \diagdown COO \end{matrix}$ , m.p.  $182^\circ$ , is obtained by con-

densation of phthalaldehydic acid with acetophenone (*Hamburger*, *Mo.* 19, 427).

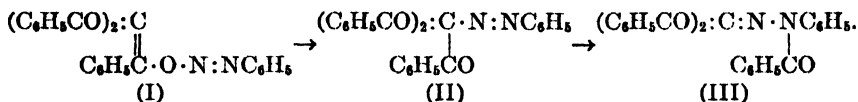
**Benzoyl-phenyl-acetylene**,  $C_6H_5COC:CC_6H_5$ , m.p.  $50^\circ$ , is obtained from sodio-phenylacetylene and benzoyl chloride in ether. It is broken down by alkalis into benzoic acid and acetophenone, and is converted by concentrated sulphuric acid into dibenzoyl-methane (*Nef*, *Ann.* 308, 276; *Moureu*, *C.r.* 130, 1259). **Phenyl-acetylene-phenyl-carbinol**,  $C_6H_5C:C\cdot CH(OH)C_6H_5$ , b.p.  $221^\circ$  (20 mm.), is obtained by the action of benzaldehyde on sodio-phenylacetylene (*Moureu*, *C.r.* 134, 355).

**Dibenzoylmethane**,  $C_6H_5CO\cdot CH_2\cdot COC_6H_5$  or  $C_6H_5C(OH):CHCOC_6H_5$  (see *Proc.* 20, 48), is obtained by boiling ethyl dibenzoylacetate with water, by condensation of ethyl benzoate with acetophenone, or by transformation of acetophenone-O-benzoate,  $C_6H_5C(OOCC_6H_5):CH_2$ , formed by heating acetophenone with benzoyl chloride, with sodium in benzene solution (*Claisen*, *Ber.* 36, 3674). It occurs almost exclusively in the enol form (*Abell*, *J.* 101, 998) and is one of the most stable keto-enol systems. It dissolves in alkali, forms a difficultly soluble copper salt, a red iron salt, and is readily attacked by permanganate. When acted upon by benzoyl chloride and pyridine it gives an *O*-benzoate,  $C_6H_5C(OCOC_6H_5):CHCOC_6H_5$ , m.p.  $109^\circ$  (*Claisen*, *Ber.* 36, 3679). Dibenzoylmethane occurs, like *p*-methyl-chalkone (p. 577), in characteristic polymorphic forms, melting at  $73^\circ$ ,  $78^\circ$ , and  $81^\circ$ . The same phenomenon is found among the ethers, which are derived from the enol form. Ethyl ether, m.p.  $63^\circ$ ,  $74^\circ$ ,  $78^\circ$ , and  $81^\circ$  (*Weygand*, *Ber.* 62, 562). Dibenzoylmethane gives, amongst other substances, an isonitroso-compound,  $(C_6H_5CO)_2C:NOH$ , with nitrous acid, from which the corresponding triketone:

**Diphenyl-triketone**,  $C_6H_5COCOCOC_6H_5$ , may be obtained. This compound forms yellow crystals, melts at  $67^\circ$ , and boils at  $289^\circ$  (175 mm.). The triketone combines with water to form a colourless hydrate, m.p.  $89^\circ$  (*de Neuville*, *Ber.* 23, 3378; *Wieland*, *Ber.* 39, 1488).

**Dibenzoyl-acetylmethane**, or **dibenzoyl-acetone**, exists in three forms, of which one is apparently the diketo-hydroxyl-form,  $(C_6H_5CO)_2C:C(OH)CH_3$  ( $\alpha$ -form, m.p.  $80^\circ$ ), and the second a triketone-form  $(C_6H_5CO)_2CH\cdot COCH_3$  ( $\beta$ -form, m.p.  $107-110^\circ$ ). When these are treated with acetyl chloride they are converted into an unstable  $\gamma$ -form, of which the m.p. is above  $142^\circ$  (*Michael*, *Ann.* 390, 46). It is obtained from benzoyl-acetone and benzoyl chloride by the action of caustic soda. From dibenzoylmethane, **tribenzoylmethane**,  $(C_6H_5CO)_3CH$ , m.p.  $225^\circ$ , is obtained. By boiling with potash and ethyl acetate the keto-form is converted into the alkali-soluble enol-form,  $(C_6H_5CO)_2C:C(OH)C_6H_5$ , m.p.  $210-216^\circ$  (*Abell*, *J.* 101, 1029). The latter combines with 1 mol. of phenyl-diazonium

chloride to give a yellow diazo-hydroxy-compound (I), m.p. 125°, which is readily decomposed by acids. When heated it is first converted into a red C-azo-compound (II), m.p. 164°, and stable towards acids, and then into the colourless benzoyl-phenylhydrazone of diphenyltriketone (III), m.p. 203°, migration of a benzoyl group having taken place (*Dimroth*, Ber. 41, 4012):



This process corresponds to the conversion of aliphatic-aromatic azo-compounds into aryl-hydrazones (p. 152), and is a reversal of the transformation of quino-acyl-phenylhydrazones into O-acylated hydroxyazo-compounds (p. 210).

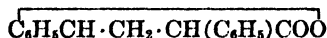
**Carboxylic acids:**—**Dibenzylacetic acid**,  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{CHCOOH}$ , m.p. 78°, is obtained from  $\alpha$ -benzyl-cinnamic acid,  $\text{C}_6\text{H}_5\text{CH:CH}(\text{C}_6\text{H}_5)\text{COOH}$ , m.p. 159°, which is itself the condensation product of benzaldehyde and hydrocinnamic acid, by reduction with sodium amalgam (*Schmid*, J. pr. [2], 62, 545). It can also be obtained from dibenzyl-malonic acid,  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}(\text{COOH})_2$ , of which the ester is obtained by benzylating diethyl malonate. *o,o'*-Dinitrodibenzyl-acetic acid,

$\text{C}_6\text{H}_4\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\ \text{NO}_2 \quad \text{COOH} \quad \text{O}_2\text{N} \end{array}\text{C}_6\text{H}_4$ , prepared in the same manner, condenses to tetrahydronaphtholine on reduction with zinc dust (*Reissert*, Ber. 27, 2248; 29, 636; cf. *Romeo*, Gazz. 32, 355). **Dibenzylmalononitrile**,  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}(\text{CN})_2$ , m.p. 130°, b.p. 360°, is obtained from the corresponding nitrile-amide, which can be obtained from cyanoacetamide. **Dibenzylethylamine**,  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{CHCH}_2\text{NH}_2$ , (hydrochloride, m.p. 190°) is obtained by reduction of the nitrile with sodium and alcohol, a cyanogen group being split off (*Errera*, Gazz. 26, II, 220).

**Dibenzyl-glycolic acid**,  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}(\text{OH})\text{COOH}$ , m.p. 156°, is obtained by hydrolysis of its nitrile, the HCN addition product of dibenzyl-ketone. It is also obtained by boiling vulpinic acid or pulvinic acid with alkalis. With concentrated caustic potash it breaks down on warming into oxalic acid and toluene (*Spiegel*, Ann. 219, 41).

$\alpha$ -**Phenyl- $\beta$ -benzoyl-propionic acid**,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{COOH}$ , m.p. 153°. The nitrile of this acid, m.p. 127°, is obtained by the action of potassium cyanide on chlorobenzyl-acetophenone and its ester is obtained from phenyl-succinic-methyl ester acid chloride by the action of benzene and aluminium chloride. When the acid is heated with acetic anhydride it gives a lactone of the isomeric

$\alpha$ -**diphenyl- $\gamma$ -hydroxycrotonic acid**  $\text{C}_6\text{H}_5\text{C:CH}\cdot\text{CH}(\text{C}_6\text{H}_5)\text{COO}$ , m.p. 110°, and on reduction with sodium,  $\alpha,\gamma$ -**diphenylbutyrolactone** (*Anschütz*, *Montfort*, Ann. 284, 1):



$\alpha,\gamma$ -**Diphenylaceto-acetic acid** is isomeric with  $\alpha$ -phenyl- $\beta$ -benzoylpropionic acid. Its ester,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CH}_2\cdot\text{COOH}$ , m.p. 79°, is obtained by condensation of two molecules of ethyl phenyl-acetate by means of sodium ethylate. The ester is converted into a naphthalene derivative, phenyl-naphtho-resorcinol by treatment with concentrated sulphuric acid (*Volhard*, Ann. 296, 1).

$\beta$ -**Phenyl- $\gamma$ -benzoylbutyric acid**,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CH}_2\cdot\text{COOH}$ , m.p. 153°, is obtained by the action of acetophenone on ethyl cinnamate in the presence of sodium ethylate, and also by the transformation of the reaction product of diethyl malonate and benzylidene-acetophenone (*Stobbe*, Ber. 34, 653).

**Benzylidene-benzoylacetic ester**,  $\text{C}_6\text{H}_5\text{CH:C}(\text{COOC}_2\text{H}_5)\cdot\text{COC}_6\text{H}_5$ , m.p. 98°, is obtained from benzaldehyde, benzoylacetic ester, and piperidine (*Ruhemann*, Proc. 19, 128; *Bertini*, Gazz. 33, II, 145).

**Dibenzoylacetic acid**,  $(\text{C}_6\text{H}_5\text{CO})_2\text{CHCOOH}$  or  $\text{C}_6\text{H}_5\text{C}(\text{OH})=\text{C}(\text{C}_6\text{H}_5\text{CO})\cdot\text{COOH}$ , m.p.

109°. The ester of this acid is obtained from benzoyl-acetic ester by the action

of benzoyl chloride. When dry distilled, the ester loses carbon dioxide and gives  $\alpha$ -hydroxybenzylidene-acetophenone, and on warming with dilute sulphuric acid it gives acetophenone, carbon dioxide and benzoic acid. Its nitrile is obtained from cyanoacetophenone by the action of benzoyl chloride, and shows powerful acidic properties. The silver salt reacts with methyl iodide giving a methyl ether,  $C_6H_5COC(CN):C(OCH_3)C_6H_5$ , m.p. 118°, and with benzoyl chloride giving tribenzoyl-acetonitrile,  $(C_6H_5CO)_3C \cdot CN$  or  $C_6H_5COC(CN):C(OOCC_6H_5)C_6H_5$ , (m.p. 138°) (*Seidel*, J. pr. [2], 58, 151).

$\gamma$ -Phenyl- $\beta$ -benzylidene- $\alpha$ -ketobutyrolactone, 
$$\begin{array}{c} C_6H_5CH-O \\ | \\ C_6H_5CH:C-CO \end{array} \begin{array}{c} \diagup CO \\ \diagdown CO \end{array}$$
, m.p.

167°, occurs in yellow crystals. It is obtained by condensation of 2 mols. of benzaldehyde with pyruvic acid in the presence of HCl gas (*Erlenmeyer*, Ber. 32, 1450; 34, 817). When reduced with sodium amalgam it gives  $\gamma$ -phenyl- $\beta$ -benzylketobutyrolactone, which exists in two modifications, m.p. 134° and 137°, respectively (also obtainable from benzylpyruvic acid and benzaldehyde). The isomeric  $\beta$ -phenyl- $\gamma$ -benzyl- $\alpha$ -ketobutyrolactone, m.p. 171°, is formed from 2 mols. phenylpyruvic acid with loss of carbon dioxide (*Erlenmeyer*, Ber. 35, 1942).

$\gamma$ -Benzyl- $\gamma$ -benzylidenepyrotartaric acid, 
$$\begin{array}{c} C_6H_5CH_2 \\ | \\ C_6H_5CH \end{array} \begin{array}{c} \diagup C-CH \\ \diagdown C-CH \end{array} \begin{array}{c} \diagup COOH \\ \diagdown CH_2COOH \end{array}$$
, m.p.

147°. The ester of this acid is obtained by condensation of dibenzyl-ketone (p. 576) and ethyl succinate in the presence of sodium ethylate (*Russwurm*, Ann. 308, 175).

$\gamma$ -Phenyl- $\gamma$ -phenacylpyrotartaric acid, 
$$\begin{array}{c} C_6H_5COCH_2 \\ | \\ C_6H_5 \end{array} \begin{array}{c} \diagup CH-CH \\ \diagdown CH-CH \end{array} \begin{array}{c} \diagup CH_2COOH \\ \diagdown COOH \end{array}$$
, is

obtained from ethyl succinate and benzalacetophenone with sodium ethylate. Its dimethyl ester readily condenses further to a pentacarboxylic\* diketocarboxylic ester, 
$$\begin{array}{c} C_6H_5CO \cdot CH \cdot CO \cdot CH_2 \\ | \\ C_6H_5CH \end{array} \begin{array}{c} \diagup CHCOOCH_3 \\ \diagdown CHCOOCH_3 \end{array}$$
, which is readily decomposed by sodium

methylate to the acyclic dimethyl-ester (*Stobbe*, Ann. 326, 347).

Triphenyl- $\beta$ -lactic acid,  $(C_6H_5)_2C(OH)-CH(C_6H_5) \cdot COOH$ , m.p. 205–208°, is obtained from benzophenone and diphenylacetic acid under the influence of light (*Palerno*, Gazz. 40, II, 321). By removal of water it gives 1,2-diphenylindone (*de Fazi*, Atti. Accad. Linc. Roma [5], 24, I, 439).

$\alpha, \beta, \gamma$ -Triphenyl-glutaric acid,  $C_6H_5CH[CH(C_6H_5)COOH]_2$ , m.p. 237°. The nitrile of this acid, m.p. 138°, is obtained by the combination of benzalbenzylcyanide with a second molecule of benzyl cyanide (*Henze*, Ber. 31, 3059).

### (e) $\omega, \omega$ -Diphenylbutane Group

Dibenzylethane,  $\alpha, \delta$ -diphenylbutane,  $C_6H_5CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2C_6H_5$ , m.p. 52°, is produced by the reduction of  $\Delta^2$ -diphenylbutylene,  $C_6H_5CH_2 \cdot CH:CH \cdot CH_2C_6H_5$ , m.p. 45°, by means of hydriodic acid.  $\Delta^2$ -Diphenylbutylene is obtained by the action of sodium amalgam on diphenyl-butadiene or diphenylbutatriene (*Straus*, Ann. 342, 253), or from  $\alpha$ -phenyl-cinnamenyl-acrylic nitrile, by the action of sodium and alcohol (*Freund*, Ber. 23, 2857).

$\alpha, \delta$ -Diphenylbutadiene, or diphenyldiethylene,  $C_6H_5CH:CH:CH:C_6H_5$ , is known in the three theoretically possible stereoisomeric forms: the  $\alpha$ -form (*trans-trans*), m.p. 151°, the  $\beta$ -form (*cis-cis*), m.p. 70.5°, and the  $\gamma$ -form (*cis-trans*), an oil. The  $\alpha$ -form is the most stable. The two others pass into it on keeping, and rapidly on exposure to light. The  $\alpha$ -form is obtained: 1. By heating  $\alpha$ -phenylcinnamenyl-acrylic acid or dibenzalpropionic acid. 2. From the dibromide of  $\Delta^2$ -diphenylbutylene by the action of quinoline. 3. In smaller yield by the reduction of phenylacetylene with zinc dust and alcohol. 4. By the action of magnesium on  $\omega$ -bromostyrene (*Rupe*, Ber. 43, 1232). 5. By condensation of cinnamic aldehyde with phenylacetic acid (*Kuhn*, Helv. 11, 103). The  $\beta$ -form is obtained from diphenyldiacetylene, and the  $\gamma$ -form from diphenyl-butatriene (m.p. 97°) by reduction with zinc dust and alcohol (*Straus*, Ann. 342, 238).

\* Pentacyclic = with five rings; pentacarboxylic = ring with five members.

With bromine in chloroform solution, diphenylbutadiene gives a dibromide, m.p.  $141^\circ$ , which can also be obtained by the addition of 2 mols. of HBr to diphenylbutatriene, and apparently contains the bromine atoms in the 1,4-position (*Straus*, Ann. 342, 244). With two mols. of nitrogen dioxide, it combines with 1,4-addition to give diphenyl-dinitro-butylene,  $C_6H_5CH(NO_2) \cdot CH : CH \cdot CH(NO_2)C_6H_5$ , m.p.  $158^\circ$ , colourless needles, from which, by the action of alkalis, diphenyl- $\alpha$ -nitrobutadiene,  $C_6H_5C(NO_2) : CH : CH : CHC_6H_5$ , m.p.  $112^\circ$ , is obtained, nitrous acid being split off. The last-named compound forms golden-yellow tablets (*Wiand*, Ann. 360, 310).

**Diphenylbutatriene**,  $C_6H_5 \cdot CH : C : C : CH \cdot C_6H_5$ , occurs in two stereoisomeric forms, of which the stable *trans*-form, m.p.  $97^\circ$ , is obtained by partial reduction of copper phenylacetylide in glacial acetic acid with zinc dust and alcohol. The labile, *cis*-form, b.p.  $188^\circ$  (12 mm.), is obtained by a similar process from diphenyl-diacetylene. By irradiation, or the presence of a trace of iodine, the labile form passes into the stable form (*Straus*, Ann. 342, 225). Diphenylbutatriene was formerly regarded as diphenylbutenine, until ozonisation and hydrolysis gave benzaldehyde and traces of oxalic acid, when it was obvious that the compound had the triene formula (*Grignard*, C.r. 188, 1531).

**Tetraphenylbutatriene**,  $(C_6H_5)_2C : C : C : C(C_6H_5)_2$ , m.p.  $235^\circ$ , is obtained by the action of hydrogen iodide in glacial acetic acid on tetraphenylbutene-diol. On reduction it gives tetraphenylbutane, m.p.  $121^\circ$ , and is readily transformed into triphenylbenzofulvene (*Salkind*, Ber. 61, 2306).

**Diphenyl-diacetylene**,  $C_6H_5C : C : C : C_6H_5$ , m.p.  $88^\circ$ , is obtained from copper phenylacetylide,  $(C_6H_5C : C)_2Cu$ , by shaking in ammoniacal solution with air, or by the action of potassium ferricyanide (*Strauss*, Ann. 342, 223). It is the parent hydrocarbon of indigo-

blue. Its *o,o'*-dinitro-compound,  $C_6H_4 \begin{array}{c} \diagup C : C - C : C \diagdown \\ NO_2 \quad NO_2 \end{array} C_6H_4$  (obtained from *o*-nitrophenylacetylene), isomerises in the presence of concentrated sulphuric acid to di-isatogen, which, on reduction with ammo-

nium sulphide, gives indigo blue,  $C_6H_4 \begin{array}{c} \diagup CO \diagdown \\ NH \end{array} C : C \begin{array}{c} \diagup CO \diagdown \\ NH \end{array} C_6H_4$  (*Baeyer*, Ber. 15, 53).

By the action of bromine in carbon disulphide, a dibromide, m.p.  $42^\circ$ , is obtained, and a tetrabromide, m.p.  $173^\circ$ . On the other hand, bromination in ether or acetic acid solution gives tribromophenyl-naphthalene, with ring closure (*Straus*, Ann. 342, 229).

$\alpha,\alpha,\delta$ -Triphenylbutadiene,  $(C_6H_5)_2C : CH : CH : CHC_6H_5$ , m.p.  $102^\circ$ , and  $\alpha,\alpha,\beta,\delta$ -tetraphenylbutadiene,  $(C_6H_5)_2C : C(C_6H_5) : CH : CHC_6H_5$ , m.p.  $147^\circ$ , are obtained by the action of diphenyl-ketene on cinnamic aldehyde and benzalacetophenone, respectively, carbon dioxide being split off (*Staudinger*, Ber. 42, 4249).

$\alpha,\alpha,\delta,\delta$ -Tetraphenylbutadiene,  $(C_6H_5)_2C : CH : CH : C(C_6H_5)_2$ , m.p.  $202^\circ$ , is obtained from tetraphenyl-tetramethylene glycol,  $(C_6H_5)_2C(OH) \cdot CH_2 \cdot CH_2 \cdot C(OH)(C_6H_5)_2$ , m.p.  $208^\circ$ , the condensation product of ethyl succinate and phenyl magnesium bromide (*Valeur*, C.r. 136, 694).

$\alpha,\beta,\gamma,\delta$ -Tetraphenylbutadiene,  $(C_6H_5) \cdot CH : C(C_6H_5) \cdot C(C_6H_5) : CH(C_6H_5)$ , is obtained from the two stereoisomeric desoxybenzoin-pinacones, by the action of acetyl chloride. It melts at  $184^\circ$ . Its dibromide, m.p.  $176^\circ$ , gives 1-benzal-2,3-diphenylindene on boiling with acetic acid (*Orekhoff*, Ber. 47, 89).

**Ketones**.—Phenylethylbenzyl-ketone, or 1,4-diphenylbutanone-2,  $C_6H_5CH_2 \cdot CH_2COCH_2C_6H_5$ , b.p.  $234-238^\circ$  (79 mm.), is obtained in the impure state from hydrocinnamic acid by distillation with potash, and by the distillation of sodium phenylacetate and calcium hydrocinnamate. It is obtained pure by the reduction of 1,4-diphenylbutenone,  $C_6H_5CH : CHCOCH_2C_6H_5$ , m.p.  $71^\circ$ , which is produced by the alkaline condensation of benzaldehyde and phenyl-

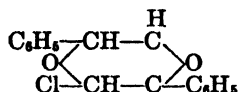
acetone (cf. p. 571 and *Goldschmidt*, Mo. 22, 659, 749).  $\omega$ -Styryl-acetophenone, phenyl-isocrotonophenone,  $C_6H_5CO \cdot CH_2CH:CHC_6H_5$ , m.p.  $93^\circ$ , is obtained by the reduction of diphenyl- $\alpha$ -nitrobutadiene with stannous chloride and hydrochloric acid. It dissolves in alkalis with formation of salts of diphenyl-hydroxybutadiene,  $C_6H_5C(OH):CH:CH:CHC_6H_5$ . It condenses with benzaldehyde to give dibenzalpropiophenone,  $C_6H_5COC(:CHC_6H_5) \cdot CH:CHC_6H_5$ , m.p.  $117^\circ$  (*Wieland*, Ber. 40, 4825). *o*-Hydroxystyrylbenzyl-ketone,  $HO[1]C_6H_4CH:CHCOCH_2C_6H_5$ , b.p.  $217-219^\circ$  (12 mm.), is obtained by the action of benzyl magnesium chloride on coumarin (*Houben*, Ber. 37, 498).

Diphenacyl,  $C_6H_5CO \cdot CH_2 \cdot CH_2 \cdot COC_6H_5$ , m.p.  $145^\circ$ , is obtained by ketonic hydrolysis of phenacylbenzoyl-acetic ester, and by reduction of dibenzoyl-ethylene and the various halogeno-diphenacyls. As a  $\gamma$ -diketone it readily gives diphenyl-furan, diphenylthiophene, and diphenylpyrrole.

1,1-Dibenzoyl-ethane,  $(C_6H_5CO)_2 \cdot CH \cdot CH_2$ , m.p.  $84^\circ$ , is obtained from phenyl- $\alpha$ -hydroxystyryl-ketone and methyl iodide in the presence of silver oxide, or from phenylethyl-ketone and ethyl benzoate in the presence of sodium (*Abell*, J. 101, 989).

*sym*-Tetrabenzoyl-ethane,  $(C_6H_5 \cdot CO)_2 \cdot CH-CH(C_6H_5CO)_2$ , m.p.  $205^\circ$ , see *Abell*, loc. cit.

$\gamma$ -Chloro- and  $\gamma$ -bromo-diphenacyl,  $C_6H_5COCHCl \cdot CH_2COC_6H_5$ , and  $C_6H_5COCHBr \cdot CH_2COC_6H_5$ , m.p.  $141^\circ$  and  $139^\circ$ , respectively, are obtained from dibenzoyl-ethylene and the halogen acids. They readily split off the halogen acids again. They react with potassium iodide giving  $\gamma$ -iododiphenacyl,  $C_6H_5COCHI \cdot CH_2COC_6H_5$ , m.p.  $121^\circ$ . Isomeric halogeno-diphenacyls are formed by the action of alcoholic potash on the phenacyl halides,  $C_6H_5COCH_2X$  (p. 404). In contrast to the above compounds, they show no ketonic or diketonic reactions, and are characterised by the ease with which they add on carboxylic halides (acetyl chloride, or bromide, etc.) and the halogen acids. They appear to be derived from a tetrahydrofuran.  $\alpha$ - and  $\beta$ -Forms exist, differing in the space arrangement (*cis-trans*) of the halogen atoms. The constitution:



is deduced in Ann. 400, 86. On reduction it gives diphenacyl.  $\alpha$ - and  $\beta$ -Chlorodiphenacyl, m.p.  $117^\circ$  and  $155^\circ$ , respectively.  $\alpha$ - and  $\beta$ -Bromodiphenacyl, m.p.  $129^\circ$  and  $161^\circ$ , respectively.

$\alpha$ -,  $\beta$ -, and  $\delta$ -Iododiphenacyl, m.p.  $82-93^\circ$  (decomp.),  $150-153^\circ$  (decomp.) and  $113^\circ$  (decomp.). If the ether solution of phenacyl iodide is treated with sodium,

tribenzoyl-cyclopropane,  $C_6H_5COCH \begin{array}{c} \diagup \text{CHCOC}_6\text{H}_5 \\ | \\ \text{CHCOC}_6\text{H}_5 \end{array}$ , is formed (*Paal*, Ber. 36, 2686, 2425).

Dibenzoyl-ethylene,  $C_6H_5COCH:CHCOC_6H_5$ , *cis*-form m.p.  $134^\circ$ , *trans*-form m.p.  $111^\circ$ , is obtained by heating dibenzoyl-malic acid (p. 586), carbon dioxide and water being split off. The *cis*-form is converted into the *trans* by means of hydrochloric acid, and the *trans*-form is converted into the *cis*- by irradiation. The *cis*-form reacts more readily than the *trans*- with hydrazine, forming diphenyl-pyridazine. It also enters into addition reactions more readily (*Paal*, Ber. 35, 168).

Tetrabenzoyl-ethylene, m.p.  $184^\circ$ , is obtained by the action of chlorine on tetrabenzoyl-ethane. It is very sensitive to light (*Halban*, Z. physikal. Chem. 96, 233).

Phenacylbenzyl-ketone,  $C_6H_5 \cdot COCH_2COCH_2C_6H_5$ , m.p.  $54-56^\circ$ , is obtained from phenylacetic ester and acetophenone by the action of sodium in ether. It is isomeric with diphenacyl (*Bülow*, Ber. 34, 1479).

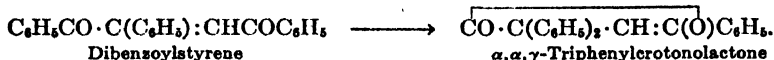
Desyl-acetophenone,  $C_6H_5CO \cdot CH(C_6H_5)CH_2COC_6H_5$ , m.p.  $126^\circ$ , is obtained by condensation of benzoin and acetophenone by means of potassium cyanide (*Smith*, J. 37, 643; Ber. 26, 60; Am. 22, 249). For the action of hydrazine, see *Smith*, Ann. 289, 310.

Bidesyl, dibenzoyl-dibenzyl,  $C_6H_5CO \cdot CH(C_6H_5)CH(C_6H_5)COC_6H_5$ , m.p.  $255^\circ$ ,

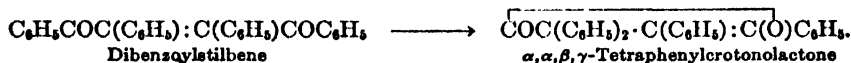


is obtained by the action of iodine on sodio-desoxybenzoin, or from desyl bromide (*Knoevenagel*, Ber. 21, 1355; 25, 285), when it is produced together with *isobidesyl*, m.p. 161°. As a 1,4-diketone it gives tetraphenylfuran, lepidene and tetraphenylpyrrole.

$\alpha,\beta$ -Dibenzoylstyrene,  $C_6H_5CO \cdot CH : C(C_6H_5)COC_6H_5$ , *cis*-form m.p. 129°, *trans*-form m.p. 198°, is obtained by the action of alcoholic potash on benzil and acetophenone. It changes, on heating into the isomeric **triphenylcrotonolactone**, m.p. 118°, a transformation involving the migration of a phenyl radical.



**Dibenzoylstilbene**, needle-shaped hydroxylepidene,  $C_6H_5CO \cdot C(C_6H_5) : C(C_6H_5)COC_6H_5$ , m.p. 220°, is obtained by the oxidation of lepidene by nitric acid, or from thionessal (p. 560) by the action of potassium chlorate and hydrochloric acid. When heated it also undergoes transformation into **tetraphenylcrotonolactone**, or table-shaped hydroxylepidene, m.p. 136°:



On reduction, dibenzoylstilbene gives *bidesyl*.

**Diphenyl-tetraketone**,  $C_6H_5COCOCOCOC_6H_5 (+H_2O)$ , m.p. 87°, is red when anhydrous, and yellow when hydrated. It is obtained by the oxidation of **benzoylformoin**,  $C_6H_5CO \cdot CO \cdot CH(OH)COC_6H_5$ , m.p. 170°, which is itself obtained from two molecules of phenyl-glyoxal under the influence of potassium cyanide, in the same way as benzoin is obtained from benzaldehyde. Benzoylformoin is also readily obtained by the action of soda on isonitroso-acetophenone acetate,  $C_6H_5COCH : NOCOCH_3$ . Substituted diphenyl-tetraketones are obtained in a similar manner (*Abenius*, Ber. 25, 3468). Diphenyltetraketone is a member of the following CO homologous series:

Diphenyl-ketone, benzophenone,  $C_6H_5COC_6H_5$  (p. 515).

Diphenyl-diketone, benzil,  $C_6H_5COCOC_6H_5$  (p. 565).

Diphenyl-triketone,  $C_6H_5COCOCOC_6H_5$  (p. 579).

Diphenyl-tetraketone,  $C_6H_5COCOCOCOC_6H_5$ .

With hydroxylamine it gives only one 1,4-dioxime,  $[C_6H_5C(NO)CO]_2$ , m.p. 176° (decomp.). The 2,3-dioxime, or dibenzoyl-glyoxime,  $C_6H_5COC(NO) \cdot C(NO)COC_6H_5$ , m.p. 108° (decomp.), is obtained by reduction of a peroxide, which is produced by the action of nitric acid on acetophenone. The 2,3-dioxime gives diphenyltetraketoxime,  $C_6H_5[C(NO)H]_2C_6H_5$ , m.p. 225°, with hydroxylamine (*Angeli*, Ber. 26, 528).

**Carboxylic acids**.—Cinnamylidene-phenylacetic acid, and dibenzalpropionic acid are derived from diphenylbutadiene.

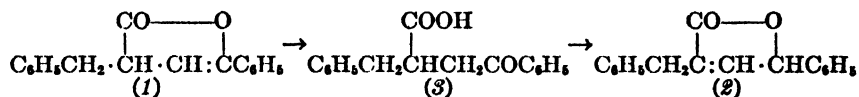
**Cinnamylidene-phenylacetic acid**, or " $\alpha$ -phenyl-cinnamenyl-acrylic acid,"  $C_6H_5C(COOH) : CH : CH : CHC_6H_5$ , m.p. 188°, is obtained from cinnamic aldehyde and phenylacetic acid. **Dibenzalpropionic acid**,  $C_6H_5CH : C(COOH) \cdot CH : CHC_6H_5$ , is obtained from benzaldehyde and styrylacetic acid (p. 469) by Perkin's method. These two diolefin-carboxylic acids have been thoroughly studied by *Thiele* from the viewpoint of the theory of conjugated double bonds (*Ann.* 306, 87-246; cf. *Hinrichsen*, Ber. 37, 1121).

" $\alpha$ -Phenyl-cinnamenyl-acrylic acid" gives a dibromide, m.p. 175° (decomp.), with bromine. This compound contains the bromine atoms in the 1,4-position, since it gives with alkali  $\alpha,\alpha$ -diphenyldihydrofuran, together with a brominated acid. On the other hand the dibromide is converted into the lactone of cornicularic acid,  $C_6H_5C(COOH) : CH \cdot COCH_2C_6H_5$ , m.p. 123°, by heating with diethylaniline (isomerisation occurring). This acid can also be obtained by reduction of vulpinic acid (p. 586). By reduction of " $\alpha$ -phenyl-cinnamenyl-acrylic acid" the first product is a 2,5-diphenylpentenic acid,  $C_6H_5CH(COOH)CH : CHCH_2 \cdot C_6H_5$ , m.p. 101°, which with alkali gives the  $\alpha,\beta$ -unsaturated acid, and with acetic-sulphuric acid gives the lactone of **tetrahydrocornicularic acid**,  $C_6H_5CH(COOH) \cdot CH_2 \cdot CH(OH)CH_2C_6H_5$ . With bromine, the 2,5-diphenylpentenic acid gives

1,3-phenylbenzyl- $\Delta^1$ -crotonolactone,  $\text{C}_6\text{H}_5\text{C}:\text{CH}:\text{CH}:\text{CH}_2\cdot\text{C}_6\text{H}_5$ , which gives hydrocornicularic acid with alkali (*Thiele*, Ann. 319, 211).

Dibenzalpropionic acid also readily gives a 1,4-dibromide, which readily passes into a bromolactone and a diolefine lactone, benzalphenylcrotonolactone,

$\text{C}_6\text{H}_5\text{CH}:\text{C}:\text{CH}:\text{CC}_6\text{H}_5$ , m.p. 150°. This gives  $\alpha$ -phenacylcinnamic acid,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{COOH})\text{CH}_2\text{COC}_6\text{H}_5$ , m.p. 171°, when treated with alkali. On reduction, the bromolactone and the diolefine lactone give a *labile* lactone (1), m.p. 101°, and a *stable* lactone (2), m.p. 67°, which both give  $\alpha$ -phenacylhydrocinnamic acid, (3), when treated with alkali (cf. also p. 570).



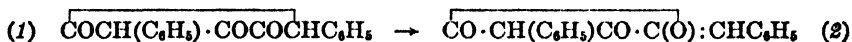
$\alpha$ -Benzylphenylisocrotonic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{CH}(\text{COOH})\text{CH}:\text{CHC}_6\text{H}_5$ , m.p. 124°, is obtained by the reduction of dibenzalpropionic acid. It is characterised by the ease with which it passes into naphthalene derivatives. With bromine, HBr is split off and phenyl-bromotetrahydronaphthoic acid is formed.

*p,p'*-Diaminodiphenyl-cyanobutadiene,  $\text{NH}_2[4]\text{C}_6\text{H}_4\text{CH}:\text{CH}:\text{CH}:\text{C}(\text{CN})\cdot\text{C}_6\text{H}_4[4]\text{NH}_2$ , m.p. 196°, is derived from the nitrile of "phenyl-cinnamenyl-acrylic acid." Like benzidine and *p,p'*-diaminostilbene it is a starting substance for the preparation of substantive cotton dyes (*Freund*, Ber. 34, 3109).

Diphenylbutadiene-acetic acid,  $\text{C}_6\text{H}_5\text{CH}:\text{CH}:\text{CH}:\text{C}(\text{C}_6\text{H}_5)\text{CH}_2\text{COOH}$ , m.p. 190°, obtained from cinnamic aldehyde and phenyl-succinic acid, gives diphenylphenol on boiling with acetic anhydride (*Fichter*, Ber. 36, 1407).

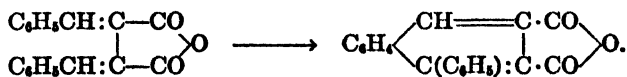
The ester of benzoylphenacyl-acetic acid, or  $\alpha,\beta$ -dibenzoylpropionic acid,  $\text{C}_6\text{H}_5\text{COCH}_2\cdot\text{CH}(\text{COC}_6\text{H}_5)\text{COOR}$ , is obtained from benzoylactic ester by the action of phenacyl bromide. By ketonic hydrolysis it gives diphenacyl, and by acid hydrolysis, benzoylpropionic acid and benzoic acid.

Isomeric with benzoyloxalylphenylacetic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{CO}\cdot\text{COCH}(\text{C}_6\text{H}_5)\cdot\text{COOH}$ , is *iso-oxalyl*dibenzyl ketone (2), m.p. 240–242°. The latter is formed by isomerisation of oxalyl-dibenzylketone (1) by heating it above its m.p. (*Claisen*, Ann. 284, 293):



Isoxalylidibenzyl ketone, like pulvinic acid which is richer in carbon dioxide, is converted by alkali into dibenzylglycolic acid,  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}(\text{OH})\text{COOH}$ .

Dibenzylidene-succinic acid,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{COOH})\cdot\text{C}(\text{COOH})\cdot\text{CHC}_6\text{H}_5$ , m.p. 201° (decomp.). Its anhydride forms lemon yellow crystals, m.p. 204°. Benzylidene- $\gamma$ -diphenyl-itaconic acid,  $(\text{C}_6\text{H}_5)_2\text{C}:\text{C}(\text{COOH})\cdot\text{C}(\text{COOH})\cdot\text{CHC}_6\text{H}_5$ , m.p. 219°; anhydride, red prisms, m.p. 218°. These acids are obtained by the condensation of ethyl succinate with 2 mols. of benzaldehyde, and with benzophenone and benzaldehyde, respectively, by means of sodium ethylate (*Stobbe*, Ber. 27, 2240). On reduction with sodium amalgam they are converted into a mixture of two stereoisomeric diphenyl- and triphenyl-butane dicarboxylic acids (*Stobbe*, Ber. 37, 2662). When irradiated dibenzylidene-succinic anhydride is converted into the anhydride of 1-phenylnaphthalene-2,3-dicarboxylic acid, dehydrogenation occurring (*Stobbe*, Ber. 40, 3374):



$\text{C}_6\text{H}_5\text{COCHCOOH}$   
Dibenzoylsuccinic acid,  $\text{C}_6\text{H}_5\text{COCHCOOH}$ ; the ethyl ester of this acid, m.p. 129°, is obtained from sodium-benzoyl-acetic ester by the action of iodine, in the

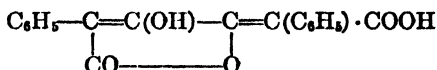
same way as ethyl diacetylsuccinate is obtained from acetoacetic ester. When water is removed from it it gives diphenylfuran-dicarboxylic ester. The ester occurs in three forms, of which the labile, alkali-soluble one is apparently the di-enol form:  $C_6H_5C(OH):C(COOH):C(COOH):C(OH)C_6H_5$ . The others correspond to the racemic and meso-forms of diketo-esters (Knorr, Ann. 293, 70).

Dibenzoylmalic ester,  $C_6H_5COCOCOOC_6H_5$ , m.p. 75°, is obtained by the action of iodine on disodio-dibenzoylsuccinic ester. On heating it isomerises to dibenzoyl-fumaric ester,  $C_6H_5OOCOCOC_6H_5$ , m.p. 88°. The maleic form condenses

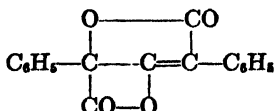
more readily with hydrazine than does the fumaric, giving diphenylpyridazine-dicarboxylic ester. The potassium salt obtained by hydrolysing the ester gives on acidifying, a hydrate of dibenzoylethylene-dicarboxylic acid, sometimes called

dibenzoylmalic acid,  $C_6H_5COC(OH)COOH$ , which loses water and carbon dioxide on heating, giving dibenzoyl-ethylene (Paal, Ber. 33, 3784).

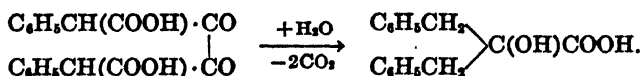
Diphenyloxal-diacetic acid, or diphenylketipinic acid,  $COOH \cdot CH(C_6H_5) \cdot COCOCH(C_6H_5)COOH$ , is isomeric with dibenzoyl-succinic acid. Its nitrile melts at 270° (decomp.), and is obtained by condensation of ethyl oxalate with two mols. of benzyl cyanide. On hydrolysis with hydrochloric or sulphuric acid, the nitrile does not give the free acid, but its anhydride, a monolactone, known as pulvinic acid:



m.p. 214°, and a dilactone:



(Karrer, Helv. 9, 446). Pulvinic acid can also be obtained from vulpinic acid,  $C_{18}H_{14}O_6$ , a compound which forms yellow prisms, m.p. 110°, by boiling with lime water. Vulpinic acid is an acid occurring in certain mosses and in the lichen *Cetraria* (*Cornicularia*) *vulpina*. When pulvinic lactone is treated with methyl alcoholic potash it is converted into vulpinic acid (Spiegel, Ann. 219, 13; Volhard, Ann. 282, 13). Vulpinic acid is therefore to be regarded as a methyl ester of pulvinic acid (Volhard, Ann. 282, 1; Wolff, Ann. 288, 14). Atromentic acid, a *p,p'*-dihydroxypulvinic acid, is obtained as the lactone, m.p. 346°, by oxidation of atromentin (p. 508) with hydrogen peroxide (Kögl, Ann. 465, 211). Pulvinic acid gives hydrocornicularic acid, or  $\alpha,\beta$ -diphenyl-laevulinic acid,  $C_6H_5CH_2CO \cdot CH_2CH(C_6H_5)COOH$ , m.p. 134°, when reduced with zinc dust and ammonia. Hydrocornicularic acid gives phenylethylbenzyl-ketone when distilled with lime, and toluene and phenyl-succinic acid when heated with caustic potash. When boiled with alkalis, pulvinic acid and vulpinic acid lose two mols. of carbon dioxide forming dibenzyl-glycolic acid. If it is supposed that diphenylketipinic acid is first formed, this reaction, apart from the splitting off of carbon dioxide, is analogous to the benzilic acid transformation:



Ethane-dibenzoyl-*o,o'*-dicarboxylic acid,  $COOH \cdot C_6H_4CO \cdot CH_2 \cdot CH_2COC_6H_4 \cdot COOH$ , m.p. 166°, is also isomeric with dibenzoyl-succinic acid. It melts at 166°,

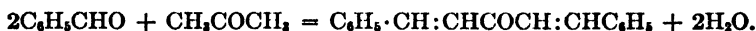
and is obtained by boiling its dilactone, ethine-diphthalyl,  $OOCC_6H_4C:CH \cdot$

$\text{CH:}\overline{\text{C}\cdot\text{C}_6\text{H}_4\text{COO}}$ , with alkalis. Ethine-diphthalyl is obtained by the condensation of two mols. of phthalic anhydride with succinic acid, carbon dioxide being split off (*Roser*, Ber. 17, 2770). It isomerises to a naphthacene derivative when acted upon by sodium ethylate.

### (f) $\omega,\omega$ -Diphenylpentane Group

1,5-Diphenylpentane is obtained by hydrogenation of 1,5-diphenylpentanol-(3) using a nickel catalyst. It boils at  $324^\circ$  (*Sabattier*, C.r. 156, 1951). 3-Diphenylmethylene-1,5-diphenylpentadiene,  $(\text{C}_6\text{H}_5\text{CH:CH})_2\text{:C:C(C}_6\text{H}_5)_2$ , sulphur-yellow needles, m.p.  $174^\circ$ , is obtained from diphenyl-ketene and dibenzal-acetone (*Staudinger*, Ber. 41, 1493).

*Ketones*.—Diolefne ketones of this group are obtained generally by the condensation of benzaldehydes (2 mols.) with ketones (1 mol.) which contain the group  $\text{—CH}_2\text{COCH}_2\text{—}$ :



Dibenzylidene-acetone, or dibenzal-acetone,  $\text{C}_6\text{H}_5\text{CH:CH}\cdot\text{COCH:CHC}_6\text{H}_5$ , yellow needles, m.p.  $112^\circ$ . The oxime, m.p.  $143^\circ$ , gives two isomeric hydroxylamino-oximes with a second molecule of hydroxylamine. Their formula is  $\text{C}_6\text{H}_5\text{CH:CHC(NOH)CH}_2\cdot\text{CH(NHOH)C}_6\text{H}_5$ , and they melt at  $165^\circ$  and  $201^\circ$ , respectively (*Minunni*, Gazz. 29, II, 387).

With hydrogen chloride, dibenzal-acetone gives not only the normal colourless addition product, but also a yellow, unstable, monohydrochloride. In solution this partly breaks down into its constituents again, and will combine with a second molecule of hydrogen chloride or metallic salts, such as ferric chloride and mercuric chloride, giving highly coloured red double compounds (*Straus*, Ber. 37, 3277; *Vorländer*, Ber. 37, 3364).

When acted upon by acetic anhydride and concentrated sulphuric acid, dibenzal-acetone loses water and is converted into diphenyl-cyclopentenolone,  $\text{C}_6\text{H}_5\text{CH—CH}_2\text{>CO}$ , m.p.  $176^\circ$  (*Vorländer*, Ber. 37, 1133; *Liebig*, Ann. 405, 188).

By the action of phosphorus pentachloride on dibenzal-acetone in benzene solution a so-called "anomalous" dibenzal-acetone dichloride,  $\text{C}_6\text{H}_5\cdot\text{CHCl—CH:—CCl—CH:CH—C}_6\text{H}_5$ , m.p.  $77^\circ$ , is obtained. In its properties and reactions it shows some analogies with triphenylchloromethane. The formation of salt-like derivatives is to be explained by the formation of carbonium ions. It dissolves in concentrated sulphuric acid giving a violet colour, and gives metallic salts with mercuric chloride, stannic chloride, etc., which are coloured double-compounds. Its reddish-violet solution in sulphur dioxide conducts electricity (*Hantzsch*, Ber. 55, 953; *Straus*, J. pr. [2], 103, 1). The chlorine atom attached to the saturated C-atom is loosely bound, and can easily be replaced by other groups, such as OH,  $\text{OCH}_3$ , etc. When treated with moist silver oxide, the very stable  $\beta$ -chlorocinnamylidene-acetophenone alcohol,  $(\text{C}_6\text{H}_5)_2\text{CH(OH)—CH:CCl}\cdot\text{CH:CH—C}_6\text{H}_5$ , m.p.  $56^\circ$ , is formed. It resembles triphenylcarbinol. Like the latter, it dissolves with a strong colour in concentrated sulphuric acid, and is very readily esterified (methyl ether, m.p.  $55^\circ$ ). With gaseous hydrogen chloride it is readily recovered into the dichloride, and with hydrogen bromide it gives a chlorobromide. In the latter it is the bromine atom that is the more reactive. On treatment of the methyl ether with sodium methylate, the second chlorine atom is replaced by methoxy. With abnormal substitution the acetal of cinnamylidene-acetophenone, m.p.  $60^\circ$ , is formed (*Straus*, Ann. 393, 235).

Benzalbenzyl-acetone,  $\text{C}_6\text{H}_5\text{CH:CHCOCH}_2\text{CH}_2\text{C}_6\text{H}_5$ , m.p.  $53^\circ$ , is obtained from benzaldehyde and benzyl-acetone by the action of caustic soda. It is reduced by sodium amalgam to dibenzyl-acetone,  $(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2)_2\text{CO}$ , b.p.  $280\text{--}285^\circ$  (120 mm.) (*Harries*, Ann. 330, 185). *p,p'*-Dinitrodibenzyl-acetone, see *Fichter*, Ber. 37, 1993.

*o*-Hydroxydibenzal-acetone, yellow leaflets, m.p.  $139^\circ$  (*Kostanecki*, Ber. 31, 728).

*o,o'*-Dihydroxydibenzal-acetone, *o*-dicoumaric-ketone, m.p. 160°. *p,p'*-Dihydroxydibenzal-acetone, m.p. 238°, orange-yellow crystals (Zincke, Ber. 36, 129; Vorländer, Ber. 62, 534). Dibenzaldieethyl-ketone, m.p. 122°, see Vorländer, Ber. 31, 1886.

Cinnamylidene-acetophenone,  $C_6H_5CH:CH:CH:CHCO_2C_6H_5$ , m.p. 103°, is obtained from cinnamic aldehyde and acetophenone, or from dibenzal-acetone through the keto-chloride. Its *oxime*, m.p. 131°, condenses on heating to  $\alpha,\alpha'$ -diphenyl-pyridine (Scholtz, Ber. 28, 1730; cf. Sorge, Ber. 35, 1065). On treatment with phosphorus pentachloride it reacts anomalously, like benzalacetophenone (p. 577) and dibenzal-acetone (p. 577) giving a keto-chloride,  $C_6H_5-CCl=CH-CH=CH-CHCl-C_6H_5$  (Straus, Ann. 393, 235).

1,3-Dibenzoylpropane,  $CH_2(CH_2COC_6H_5)_2$ , m.p. 67°, is obtained from glutaryl chloride, benzene and aluminium chloride, and also by the fission of  $\alpha,\alpha'$ -dibenzoylglutaric ester which is obtained by the action of methylene iodide or formaldehyde on ethyl benzoyl acetate. 1,1-Dibenzoylpropane,  $(C_6H_5CO)CH:CH_2-C_6H_5$ , m.p. 87°, is obtained by the action of ethyl iodide on the sodium compound of phenyl- $\alpha$ -hydroxy-styryl ketone (Abell, J. 101, 989). Dibenzoyl-diphenylpropane,  $CH_2[CH(C_6H_5)COC_6H_5]_2$ , m.p. 146°, is obtained from formaldehyde and desoxybenzoin. By reduction of these 1,5-diketones, cyclic pinacones of the cyclopentane group are obtained (Auger, Ann. chim. phys. [6], 22, 358; Wislicenus, Ann. 302, 215, 223).

1,5-Diketones of this group are obtained by condensation of benzaldehydes (1 mol.) with acetophenones (2 mols.) by means of caustic soda. Benzylidene-diacetophenone,  $C_6H_5CH(CH_2COC_6H_5)_2$ , m.p. 85° (Wislicenus, Ann. 302, 236). *o*-Hydroxybenzylidene-diacetophenone,  $(OH)[2]C_6H_4CH(CH_2COC_6H_5)_2$ , m.p. 131°. Under other conditions two molecules of benzaldehyde react with three molecules of acetophenone to give dibenzylidene-triacetophenone,  $C_6H_5CO-CH_2-CH(C_6H_5)-CH(CO-C_6H_5)-CH(C_6H_5)-CH_2-CO-C_6H_5$ , m.p. 198°, and an isomer of m.p. 256°.

Benzamarone, or benzylidene-bis-desoxybenzoin,  $C_6H_5CH[CH(C_6H_5)CO-C_6H_5]_2$ , exists in two forms, m.p. 219°, and 180° respectively. They are obtained by condensation of benzaldehyde and desoxybenzoin, and by the action of desoxybenzoin on benzylidene-desoxybenzoin in the presence of sodium ethylate. In a similar way, desoxybenzoin adds on to the unsaturated linkages of other olefine derivatives, such as  $\alpha$ -phenyl-cinnamionitrile, benzalacetacetic ester, benzal-benzoyl-pyruvic ester, etc. (Stobbe, Ber. 34, 3898). By fission of benzamarone with sodium ethylate, the sodium salt of amaric acid,  $C_{23}H_{20}O_3$ , is obtained, and with sodium isobutyrate, dimethylamaric acid is formed,  $C_{23}H_{20}O_3$  (Klingemann, Ann. 275, 50). By dry distillation, benzamarone is converted into desoxybenzoin and benzylidene-desoxybenzoin. With hydroxylamine it readily gives pentaphenyl-pyridine.

Carboxyl derivatives of the  $\omega,\omega$ -diphenyl-pentane group.— $\beta,\beta$ -Styrylphenacyl-propionic acid,  $C_6H_5CH:CH \begin{matrix} \searrow \\ \nearrow \end{matrix} CHCH_2COOH$ , m.p. 125°, is obtained from the condensation product of cinnamylidene-acetophenone (see above) and malonic ester by hydrolysis and removal of carbon dioxide. On oxidation it gives phenacyl-succinic acid,  $C_6H_5COCH_2CH(COOH) \cdot CH_2COOH$ , (Staudinger, Z. Naturwiss. 75, 433).

Diphenacylacetic acid,  $(C_6H_5COCH_2)_2CHCOOH$ , m.p. 133°, is obtained from diphenacyl-malonic ester  $(C_6H_5COCH_2)_2C(COOR)_2$ , or diphenacyl-acetoacetic ester,  $(C_6H_5COCH_2)_2C(COCH_3)COOC_2H_5$ , m.p. 83°, the products of the action of phenacyl bromide on malonic ester and acetoacetic ester, respectively. It is also formed by the alkaline condensation of acetophenone and glyoxylic acid, and by the action of cold caustic soda on benzoylacrylic acid. In the latter case, the benzoylacrylic acid first decomposes into acetophenone and glyoxylic acid (Bougault, C.r. 148, 270). As a  $\epsilon$ -diketone, diphenacylacetic acid forms a pyridine derivative with ammonia (Paal, Ber. 29, 798).

Dibenzylacetone-dicarboxylic ester,  $C_6H_5CH_2CH(COOR)COCH(COOR)CH_2-C_6H_5$ , is obtained by the benzylation of acetone-dicarboxylic ester, together with the *mono*- and *tri*-benzylated products (Fichter, Ber. 34, 1996).

Acetone-diphthalide,  $CO(CH_2CHC_6H_4[2]COO)_2$ , m.p. 137°, is obtained from

phthalaldehydic acid and acetone, acetonil-monophthalide being formed at the same time (*Hamburger, Mo. 19, 427*).

**Benzylidene-bis-benzoylactic ester**,  $C_6H_5CH[CH(COOR)COC_6H_5]_2$ , is obtained from benzalbenzoylactic ester by the action of benzoylactic ester. It is readily decomposed into its components by sodium ethylate (*Ruhemann, J. 83, 720*).

### (g) $\omega,\omega$ -Diphenylhexane Group and Higher Homologues

**1,6-Diphenyl-hexadiene**,  $C_6H_5CH:CH\cdot CH_2\cdot CH_2\cdot CH:CHC_6H_5$ , m.p.  $82^\circ$ , is obtained, together with an isomeric liquid hydrocarbon, by the action of magnesium on cinnamyl chloride,  $C_6H_5CH:CHCH_2Cl$  (*Rupe, Ber. 43, 172*). **1,1,6,6-Tetraphenyl-hexadiene**, obtained from tetraphenylhexane-diol by boiling with hydrogen chloride in glacial acetic acid, gives a potassium compound, which, on replacement of the metal by hydrogen gives  $\alpha,\alpha$ -diphenyl-propylene,  $(C_6H_5)_2C=CHCH_3$ , m.p.  $48-49^\circ$ . **1,6-Diphenyl-hexatriene**, m.p.  $200^\circ$ , greenish-yellow needles, is obtained from hydrocinnamoin (see below). Its dibromide melts at  $117^\circ$ . **Tetraphenyl-hexatriene**,  $C_6H_5CH:CH\cdot CH:CH\cdot C(C_6H_5):C(C_6H_5)_2$ , yellow prisms, m.p.  $159^\circ$ , is obtained from diphenyl-ketene and cinnamylidene-acetophenone (*Staudinger, Ber. 42, 4249*). **1,8-Diphenyl-octatetraene**, m.p.  $232^\circ$ , is obtained as chrome-yellow leaflets from succinic anhydride, cinnamic aldehyde and lead oxide in acetic anhydride. **1,1,8,8-Tetraphenyl-octadiene** (1,7), m.p.  $93^\circ$  (*Bergmann, Ber. 63, 2593*). **1,10-Diphenyl-decapentene**, m.p.  $253^\circ$ , is orange in colour. **1,12-Diphenyl-dodecahexene**, m.p.  $267^\circ$ , brownish-orange; **1,14-diphenyl-tetradecaheptene**, m.p.  $279^\circ$ , copper-bronze colour.

The above diphenyl-polyenes (*Kuhn*) are very stable, and do not polymerise. The colour is deeper the larger the number of conjugated double bonds. Up to the present stereoisomeric forms have not been discovered. Those hydrocarbons that have been prepared appear to belong to the *trans*-series. It is noteworthy that of the polyenes so far investigated, diphenyl-hexatriene is the most resistant to oxidation (*Kuhn, Helv. 11, 123*).

**Hydrocinnamoin**,  $C_6H_5CH\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH:CHC_6H_5$ , m.p.  $154^\circ$ , is obtained, together with other products, by the reduction of cinnamic aldehyde by the zinc-copper couple in alcohol (*Thiele, Ber. 32, 1296*). **Dibenzoyl-butane** (1,4), m.p.  $107^\circ$ , is obtained from adipyl chloride, benzene, and aluminium chloride. With sodamide it gives benzoyl-1-phenyl-2-cyclopentene-(1) and -(2), ring-closure occurring (*Bauer, C.r. 155, 288*). **Dibenzoyldiphenylbutadiene**,  $C_6H_5COCH:CC_6H_5$

$\begin{array}{c} | \\ C_6H_5COCH:CC_6H_5 \end{array}$ , m.p.  $192^\circ$ , is obtained from benzil and acetophenone. On reduction it gives tetraphenylbenzene (p. 509) and its derivatives (*Lehmann, Ann. 302, 195*). **Oxalyl-diacetophenone**,  $C_6H_5COCH_2COCOC_6H_5$ , m.p.  $180^\circ$ , is obtained by condensation of two mols. of acetophenone and ethyl oxalate with sodium ethylate. For reduction products of this tetraketone see *Schmidt, Ber. 28, 1206*.

$\omega,\omega$ -Diphenyldiketohexane,  $(C_6H_5COCH_2CH_2)_2$ , diphenyldiketo-octane,  $(C_6H_5COCH_2CH_2CH_2)_2$ , and diphenyldiketnonane,  $(C_6H_5COCH_2CH_2CH_2)_2CH_2$ , are obtained from the chlorides of adipic, sebacic, and azelaic acids with benzene and aluminium chloride (*Etair, Ann. chim. phys. [7], 9, 299*). **Cinnamylidene-benzylidene-acetone**,  $C_6H_5CH:CH\cdot CH:CHCOCH\cdot CHC_6H_5$ , m.p.  $106^\circ$ , is derived from a  $\omega,\omega$ -diphenylheptane. It is obtained from cinnamylidene-acetone and benzaldehyde (*Staedel, Ber. 29, 615*). **Dicinnamylidene-succinic anhydride**,  $C_6H_5CH:CH\cdot CH:C\cdot CO$

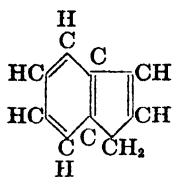
$\begin{array}{c} | \\ C_6H_5CH:CH\cdot CH:C\cdot CO \end{array} \begin{array}{c} | \\ O \end{array}$ , m.p.  $215^\circ$ , cinnabar-red needles, is obtained by the condensation of cinnamic aldehyde and sodium succinate in the presence of acetic anhydride (*Fittig, Ann. 331, 167*).

### C. Condensed Nuclei

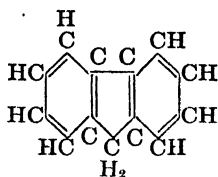
The condensed nuclei to be discussed in this section are characterised by the fact that in them C atoms of benzene nuclei participate in the formation of other carbocyclic rings.

In earlier chapters, many substances with a bicyclic structure were discussed. It may be pointed out that the capacity for forming bicyclic combination is often observed with the alicyclic compounds. On account of the plane structure of the benzene ring, the attachment of a second ring to the aromatic nucleus can, in general, only take place in the 1,2-position. Only rings with a higher number of members can attach themselves in the 1,3- or 1,4-positions (*Ziegler, Ann. 511, 1*).

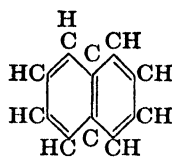
In this chapter we shall deal first with the following condensed ring systems:



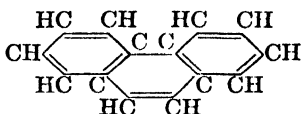
Indene



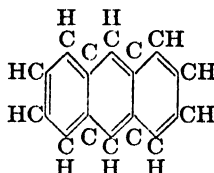
Fluorene



Naphthalene



Phenanthrene

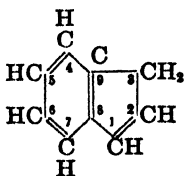


Anthracene

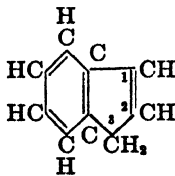
In addition to these important parent substances a large number of other condensed systems will be mentioned, which are derived from the above fundamental types by the attachment of five- or six-membered rings.

Condensed aromatic compounds show in general the behaviour of the simple benzene derivatives; but because of their particular structure they show a number of small deviations from the characteristic properties of benzene derivatives. By the appropriate oxidation they are converted, like the benzene homologues, into benzene-carboxylic acids. The parent hydrocarbons of these groups occur, like benzene, chiefly in coal-tar, from which they are obtained in greater or lesser amounts. Naphthalene and anthracene are the most important technically.

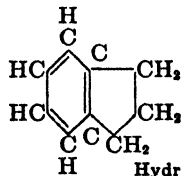
#### 1. INDENE AND HYDRINDENE GROUP



or



Indene

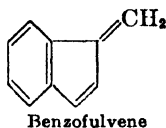


Hydrindene

Indene received its name from indole, which was discovered earlier, and which it resembles in structure. If NH is substituted for the methylene group of indene, the formula of indole is obtained.

**Indene**,  $C_9H_8$ , m.p.  $-2^\circ$ , b.p.  $182.3^\circ$ ,  $d_4^{20}$  1.0002,  $n_D^{20}$  1.5773, occurs, together with coumarone, which it resembles in its behaviour to a considerable extent, in that fraction of coal-tar boiling between  $175$  and  $185^\circ$  (Markwald, Ber. 28, 114). It can be extracted from it by means of its sodium salt, obtained by heating the coal-tar fraction with sodium or sodamide (Weissgerber, Ber. 42, 569; Spilker, Ber. 42, 572). Another method of purifying it depends on the difficultly soluble picrate, m.p.  $96^\circ$  (Kraemer, Ber. 23, 3277). Considerable quantities of indene are obtained when coal-gas is cooled (Dennstedt, Ber. 28, 1331). It is obtained by the pyrogenic condensation of acetylene, and from the synthetically prepared hydrindene-carboxylic acid by distillation of its calcium salt (Perkin, J. 65, 228). The most convenient method is by heating 1-hydrindamine hydrochloride (Kipping, Proc. 16, 54). Indene is autoxidisable, and readily polymerises. Even at ordinary temperatures and in the dark, and more rapidly in the presence of sulphuric acid, kieselguhr, or metallic halides, such as stannic chloride, it gives polyindene, which has a varying molecular weight according to the catalyst and reaction temperature. The polymers are not crystalline, and still contain one double bond per molecule of indene, so that they can be hydrogenated to polyhydrindenes. For the constitution of these compounds, see Whithy, Am. 50, 1160; Staudinger, Helv. 12, 934. Indene combines with chlorine and bromine to form dibromo- and dichloro-hydrindenes. Like the terpenes it combines with nitrosyl chloride and nitrogen trioxide to give indene-nitrosochloride and indene-nitrosite,  $\alpha$ -form m.p.  $108^\circ$  (decomp.),  $\beta$ -form m.p.  $137^\circ$  (Dennstedt, Ber. 28, 1331). On treatment with sodium and alcohol, indene is reduced to hydrindene. By heating to redness, two molecules of indene condense to chrysene, with the splitting off of four atoms of hydrogen (p. 692).

The hydrogen atoms of the  $CH_2$  group are reactive, like those of cyclopentadiene. The formation of a sodium salt on heating with sodium or sodamide has already been mentioned. It combines with ethyl oxalate in the presence of sodium ethylate to give indene-oxalic ester. With aldehydes, and (though with rather greater difficulty) with ketones, intensely coloured hydrocarbons, derivatives of benzofulvene, are formed by alkaline condensation:

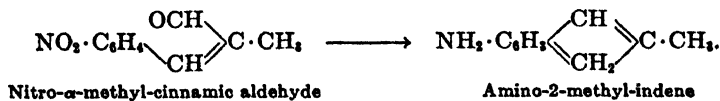


**Isomerism of indene derivatives.**—Positions 1, 2, and 3 of indene are not equivalent. Three position-isomeric substitution products of indene would therefore be expected when the substituents are in the five-membered ring. It has, however, been shown that the 3-derivatives of indene very readily pass into the 1-derivatives. This fact led to the erroneous conclusion that both 1- and 3-derivatives could not exist owing to an "oscillation of the double bond in the five-membered ring of indene" (Thiele, Ann. 347, 249).

Derivatives of indene can be synthesised by the following methods, which are reminiscent of those used for the cyclopentanes:

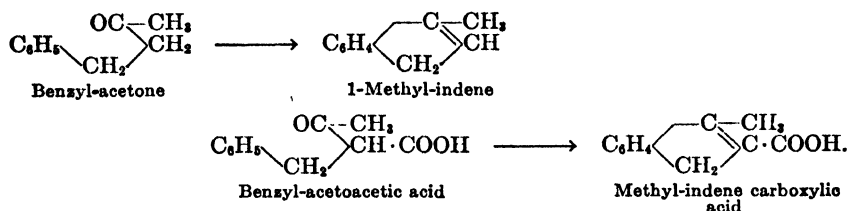
1. Benzene derivatives with the grouping condense to indene derivatives with loss of water:

(a) Nitro- $\alpha$ -alkyl-cinnamic aldehydes give on reduction amino-2-alkyl-indenes (Miller, Ber. 22, 1830)

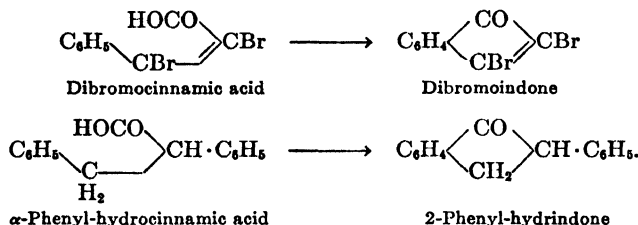




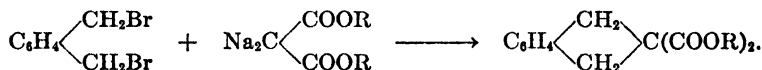
In a similar way, when benzyl-acetone and benzyl-acetoacetic ester are warmed with sulphuric acid, 1-methyl-indene and 1-methyl-indene-2-carboxylic acid are formed (Roser, Ber. 20, 1574; Ann. 247, 157):



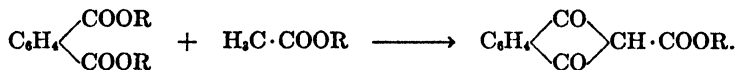
(b) When substituted cinnamic acids are treated with hot sulphuric acid or phosphorus pentoxide, indone derivatives are formed (Bakunin, Gazz. 30, II, 340). Halogen- and nitro-substituted alkylated hydrocinnamic acids (whether alkylated in the nucleus or the side-chain) give dihydroindones. Cinnamic acid and hydrocinnamic acid themselves react in the same way as cinnamic aldehyde (Roser, Ann. 247, 140; Miller, Ber. 25, 2095; Liebermann, Ber. 25, 2129; 31, 2095):



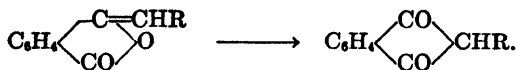
2. Derivatives of hydrindene are obtained like those of cyclobutane and cyclopentane, by the action of *o*-xylylene halides on diethyl malonate or acetoacetic ester and sodium ethylate (Baeyer, Ber. 17, 125; Scherks, Ber. 18, 378):



3a. The formation of 1,3-diketohydrindenes from ethyl phthalate and aliphatic esters or ketones corresponds to the condensation of ethyl oxalate to cyclopentane derivatives (Wislicenus, Ann. 252, 72; Schwerin, Ber. 27, 104; Wislicenus, Ann. 277, 362):

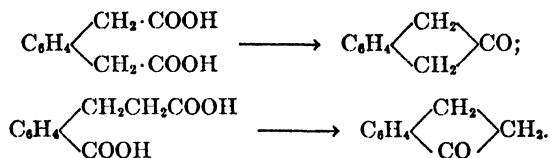


3b. The phthalide compounds,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}=\text{CHR} \\ \diagdown \text{O} \\ \text{CO} \end{array}$ , obtained by the action of aliphatic acids on phthalic anhydride are converted by sodium ethylate into the sodium compounds of the isomeric diketo-hydrindenes (Gabriel, Ber. 26, 954; Nathanson, Ber. 26, 2576; Eibner, Ber. 39, 2202):

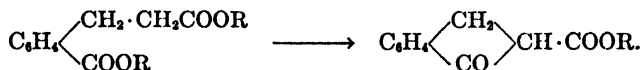


4a. The formation of hydrindones by the distillation of salts of *o*-phenylene-acetic acid and hydrocinnamic-*o*-carboxylic acid, corresponds to the formation of

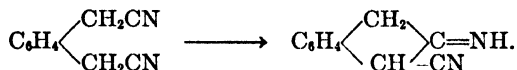
cyclic ketones from dicarboxylic acids of the adipic series (*Schad*, Ber. 26, 222; *Wislicenus*, Ber. 26, R 708):



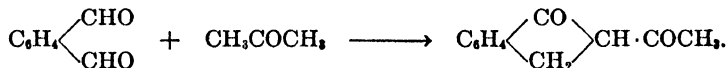
4b. By the action of sodium or sodium ethylate on the esters of *o*-phenylene-diacetic acid or hydrocinnamic-*o*-carboxylic acid gives rise to hydrindone carboxylic esters, in an analogous way to the cyclic acetoacetic condensation:



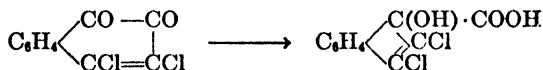
In a similar way 1-cyano-2-imino-hydrindene is obtained from *o*-phenylene-diacetonitrile by the action of sodium ethylate (*Moore*, Proc. 24, 12; *J.* 93, 165):



5. Hydrindone derivatives are formed by the alkaline condensation of phthalaldehyde with methyl-ketones and methyl-ketocarboxylic acids (*Thiele*, Ann. 347, 112; 369, 287):



6. The formation of indene derivatives from naphthalene derivatives should be specially noted. Here a six-membered ring is converted into a five-membered one, just as cyclopentadiene derivatives are formed from benzene derivatives, and fluorene derivatives are obtained from phenanthraquinone, etc. The transformations occur by the action of chlorine or hypochlorous acid on naphthols, naphthaquinones, aminonaphthols, etc. Keto-derivatives of hydronaphthalene with the group CO·CO, or CO·CCl<sub>2</sub> are first formed, which then undergo fission (*Zincke*, Ber. 20, 2890; 21, 2719). Thus dichloro-1,2-naphthaquinone gives dichloro-hydroxyindene-carboxylic acid (benzilic acid transformation):

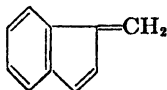


Dichloro-1,2-naphthaquinone      Dichloro-hydroxyindene carboxylic acid

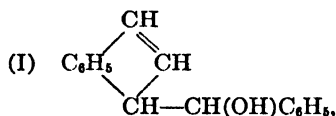
**INDENE DERIVATIVES:** 1-Methyl-indene, C<sub>6</sub>H<sub>4</sub>·C<sub>3</sub>H<sub>3</sub>·CH<sub>3</sub>, b.p. 206°, is obtained by methylation of sodio-indene, and synthetically from benzyl acetone. It can also be obtained from its carboxylic acid by splitting off carbon dioxide. 1,2-Dimethyl-indene, b.p. 112°, (19 mm.); picrate, m.p. 11°. 1,3-Dimethyl-indene, b.p. 212-214°; picrate, m.p. 95°. 1-Ethyl-indene, b.p. 215-216°; 1-allyl-indene, b.p. 138° (27 mm.); 1-benzyl-indene, m.p. 33-34°, b.p. 179° (11 mm.), C<sub>6</sub>H<sub>4</sub>:C<sub>3</sub>H<sub>3</sub>·CH<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>; 1,3-dibenzyl-indene, C<sub>6</sub>H<sub>4</sub>·C<sub>3</sub>H<sub>3</sub>(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, m.p. 63°, obtained by the benzylation of indene, and by the reduction of benzylbenzylidene-indene, m.p. 137°, with aluminium amalgam (*Thiele*, Ann. 347, 262; *Wislicenus*, Ann. 436, 10). 1-Phenyl-indene, m.p. 23°, b.p. 153-154° (14 mm.), is obtained from indanone-1 and phenyl magnesium bromide. 2-Phenyl-indene, m.p. 167° (*Mayer*, Ber. 54, 1398). For further methods of preparation, see *Roger*, Ber. 62, 1059. 3,3-Diphenyl-indene, m.p. 91-92° (*Gagnon*, Ann. chim. [10], 12, 296); 1,2-diphenyl-indene, m.p. 108° (*Thiele*, Ann. 393, 61; *Ruggli*, Ann. 414, 125; *Roger*, Ber. 62, 272) is obtained by the isomerisation of 2,3-diphenyl-indene, m.p. 118°, with alkali (*Ruggli*, Ann. 414, 125; *Orechoff*, Bull.

[4], 31, 253); 1,3-diphenyl-indene, m.p. 71–72° (Ber. 57, 1983). 1,2,3-Triphenyl-indene, m.p. 135° (Köhler, Am. 40, 217). 1,3,3-Triphenyl-indene, m.p. 135° (Vorländer, Ber. 39, 1030). 6-Amino-2-methyl-, -ethyl-, -isopropyl indene, m.p. 98°, 89°, and 84°, respectively.

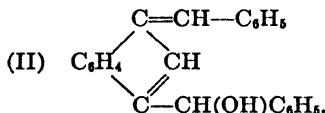
**BENZOFULVENES.** 3-Methylene-indene, or benzofulvene, m.p. 37°, b.p. 134° (10 mm.),



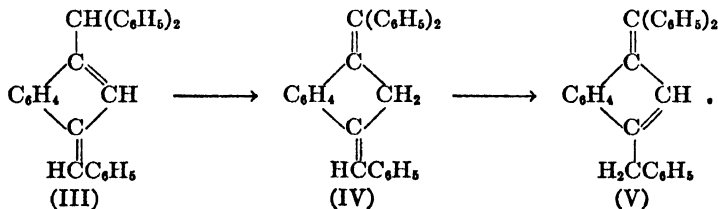
is obtained by removing hydrogen from benzofulvanol. It readily polymerises and is autoxidisable. It is peculiar that the semi-cyclic double-bond does not add on bromine (Bergmann, Ber. 64, 1481). Benzofulvanols are obtained by the decomposition of indene-magnesium halides with aldehydes or ketones. 3-Benzylidene-indene, or  $\omega$ -phenylbenzofulvene, m.p. 88°, yellow leaflets, is formed by removing hydrogen from 3-hydroxybenzyl-indene (I),



which is itself formed by the condensation of indene and benzaldehyde. It readily transforms into 1-hydroxybenzylidene-indene, which can now react a second time with benzaldehyde. 1-Hydroxybenzyl-3-benzylidene-indene (II), m.p. 135°, is thus formed in yellow crystals:



3-Cinnamylidene-indene, m.p. 190°, yellowish-red needles. 1-Substituted benzofulvenes can exist in an isomeric form which is formed by a displacement of the double bonds under the influence of alkali. Thus,  $\omega$ -phenyl-1-benzhydrylbenzofulvene (III) will become  $\omega,\omega'$ -diphenyl-1-benzylbenzofulvene (V). Another form (IV) may also occur intermediately, and has, in some cases, been isolated (Thiele, Ann. 415, 257; Bernthsen, Ann. 415, 274; Wuest, Ann. 415, 291). 3,3'-Di-indenyl, m.p. 99–100°, is obtained by the action of iodine on 3-indene-magnesium halides (Grignard, C.r. 154, 361):



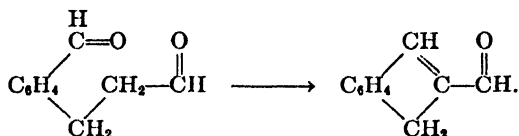
3-Bromoindene, b.p. 126° (22 mm.), is obtained by the action of cyanogen bromide on 3-indene magnesium halides. With bromine it gives a tribromoindane, m.p. 133–134° (Grignard, C.r. 154, 361).

A 5-bromoindene,  $C_6H_3Br(C_6H_4)$ , b.p. 243°, is formed by the action of bromine on hydrindene (Perkin, Ber. 26, 2251). It gives 4-bromophthalic acid on oxidation. By the action of bromine in cold chloroform on hydrindene, 1,5-dibromoindene, m.p. 32°, b.p. 143.5–144.5° is formed. For other bromo- and polybromoindenes see Jacobi, J. pr. [2], 129, 55.

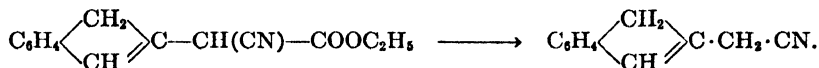
2-Nitroindene,  $C_6H_4:C_6H_4NO_2$ , m.p. 141°, yellow crystals, is obtained by dis-

tillation of indene-nitrosite with steam. It is reduced by zinc dust and glacial acetic acid to 2-hydrindone-oxime (*Wallach*, Ann. **336**, 1).

**Indene-2-aldehyde**, m.p. 50–51°, is obtained from the dialdehyde of hydrocinnamic-*o*-carboxylic acid by the action of 10% sulphuric acid (*von Braun*, Ber. **56**, 2139):



**Indene-3-nitrile**, b.p. 140–142° (14 mm.), is obtained by the action of cyanogen chloride on indene magnesium halides. On hydrolysis it gives chloro-imino-ether of **indene-3-carboxylic acid** (*Grignard*, C.r. **154**, 361). This acid can also be obtained from sodio-indene and carbon dioxide (*Weissgerber*, Ber. **44**, 1440). Indene-nitriles, which contain the CN group in the side-chain, can readily be obtained from hydrindones by condensation with cyanoacetic ester and hydrolysis with sodium ethylate. **Indenyl-2-acetonitrile**, m.p. 18°, **indenyl-2-propionitrile**, m.p. 118° (*Ingold*, J. **115**, 143):



**Indene-1-carboxylic acid**, m.p. 70°, is obtained from 1-bromoindene by combination with carbon dioxide, brought about by the Grignard reaction (*Jacobi*, J. pr. [2], **129**, 55).

**Indene-2-carboxylic acid**,  $\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_3\cdot\text{COOH}$ , m.p. 222–230°, is obtained by the action of bromine on hydrindene-2-carboxylic acid. **1-Methyl-indene-2-carboxylic acid**, m.p. 200°, is obtained from benzylacetoacetic ester.

**Indene-1,2-dicarboxylic acid**, decomposes at 215°, is obtained from benzyl-oxalacetic ester by removal of water and hydrolysis. Diethyl ester, m.p. 78° (*Bougault*, C.r. **159**, 745).

**Indene-3-oxalic acid ethyl ester**,  $\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_3\cdot\text{COCOOC}_2\text{H}_5$ , m.p. 87°, orange-red needles, is obtained from indene, ethyl oxalate and sodium ethylate. When reduced with aluminium amalgam it gives **indene-3-hydroxyacetic ester**,  $\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_3\cdot\text{CH}(\text{OH})\text{COOC}_2\text{H}_5$ , b.p. 172° (13 mm.). **Benzofulvene-carboxylic acid**,  $\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_2\cdot\text{CHCOOH}$ , decomposing at 175°, orange-yellow leaflets, is formed from the latter by hydrolysis and removal of water. When benzofulvene-carboxylic acid is reduced, **indene-1-acetic acid**,  $\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_3\cdot\text{CH}_2\text{COOH}$ , m.p. 96°, is formed, which by successive condensation with ethyl oxalate, reduction, hydrolysis, and dehydration gives  **$\omega$ -carboxybenzofulvene-1-acetic acid**,  $\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}(\text{:CHCOOH})\text{CH}_2\text{COOH}$ , m.p. about 245° (decomp.) (*Thiele*, Ann. **347**, 275).

**1,2-Dichloro-3-hydroxyindene carboxylic acid**, m.p. 100°, is obtained from dichloro- $\beta$ -naphthaquinone; it is oxidised to dichlorindone by chromic acid, and on heating with concentrated sulphuric acid it is converted into chlorindone-carboxylic acid (*Zincke*, Ann. **283**, 341).

Ketonic derivatives of indene are called the **indones**. They give an emerald green colour with concentrated sulphuric acid, which, however, is also given by indene and 2,4-diphenyl-indene (*de Fazi*, Gazz. **51**, I, 164). Alkylated indones are obtained from  $\alpha$ - and  $\beta$ -alkylcinnamic acids by the action of sulphuric acid. They are yellow to orange-coloured oils or crystals, which very readily decompose.

**1-Methyl-indone**, b.p. 140–141° (19 mm.). **2-Methyl-indone**, m.p. 47–47.5°. **1-Ethyl-indone**, m.p. 43.5° (Ber. **55**, 981). **1-Phenyl-indone**, m.p. 69–71°, is obtained in small yield by the action of sulphuric acid on  $\beta,\beta$ -diphenyl-lactic ester (*Fazi*, Gazz. **49**, II, 253).

1,2-Diphenyl-indone,  $\text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)=\text{CHCO}$ , m.p.  $151^\circ$ , forms purplish-

red crystals, and is obtained, together with triphenylacrylic acid (p. 573), by the condensation of benzophenone chloride with ethyl phenylacetate. On reduction it gives triphenylpropane, and on fusion with caustic potash it gives  $\alpha,\beta$ -diphenylvinyl-*o*-benzoic acid, from which it can be re-obtained, with triphenylacrylic acid, by heating with zinc chloride (*Meyer*, Ber. 30, 1281).

It is also obtained from the dibromide of benzylidene-desoxybenzoin by heating to  $140\text{--}150^\circ$  (*Orechoff*, Bull. [4], 25, 597) or by the action of phenyl magnesium halides on benzal-phthalide (*Weiss*, Ber. 58, 2736). The latter method can also be used for the preparation of various substituted dialkyl-indones.

2-Phenyl-*o*-, *m*-, and *p*-nitro-indone,  $\text{NO}_2\text{C}_6\text{H}_4\text{C}(\text{C}_6\text{H}_5)=\text{CHCO}$ , m.p.  $139^\circ$ ,  $205^\circ$ , and  $215\text{--}217^\circ$ , respectively, are obtained from *o*-, *m*-, and *p*-nitrophenyl- $\alpha$ -phenylcinnamic acids (*Bakunin*, Gazz. 30, II, 340).

Indone-2-acetic acid,  $\text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)=\text{CHCOCH}_2\text{COOH}$ , m.p.  $99^\circ$ , lemon-yellow prisms, is obtained by the action of concentrated sulphuric acid on phenylitaconic acid. By further treatment with mineral acid it is converted into the saturated, colourless lactone, m.p.  $123^\circ$  (*Schmidt*, Ber. 41, 3983). In a similar way, 1-methyl-, 1-phenyl-indone-2-acetic acid, and 1-phenylindone-2-propionic acid m.p.  $155^\circ$ ,  $167^\circ$ , and  $168^\circ$ , respectively, are obtained from methylphenylitaconic acid, diphenylitaconic acid, and  $\alpha$ -methyl- $\gamma,\gamma$ -diphenylitaconic acid, respectively.

1-Bromoindone,  $\text{C}_6\text{H}_4(\text{COBr})=\text{CH}_2$ , m.p.  $64^\circ$ , 1,2-dichloro- and -dibromo-indone,  $\text{C}_6\text{H}_4:\text{C}_2\text{Br}_2\text{O}$ , m.p.  $90^\circ$  and  $123^\circ$ , have been obtained synthetically from monobromo-, dichloro-, and dibromo-cinnamic acids (*Lanser*, Ber. 32, 2477; *Schlossberg*, Ber. 33, 2426). The 1-halogen atom in these substances is readily replaced by OH or NHR on warming with caustic soda and aliphatic or aromatic amines, respectively. 2-Chloro- and 2-bromo-1-hydroxyindone, m.p.  $114^\circ$  and  $119^\circ$ , respectively. 1-Anilino-indone, m.p.  $205^\circ$  (decomp.), is converted by hydrochloric acid into diketohydrindene (p. 599). One halogen atom also reacts with sodium-malonate ester, sodium-acetoacetic ester, etc. The substances produced,  $(\text{C}_6\text{H}_4\text{BrO})\text{CH}(\text{COOC}_2\text{H}_5)_2$ , m.p.  $130^\circ$ , and  $(\text{C}_6\text{H}_4\text{BrO})\text{CH}(\text{COCH}_3)\text{COOC}_2\text{H}_5$ , readily with m.p.  $81^\circ$ , are pale yellow in colour, but with alkalis become a beautiful purplish red, the solution recalling that of cochineal (*Liebermann*, Ber. 31, 2079, 2903; *Lanser*, Ber. 33, 2418; *Schlossberg*, Ber. 33, 2425). For the action of sodium ethylate on dichloro- and dibromo-indones, see Ber. 35, 2938.

Perchloroindone,  $\text{C}_6\text{Cl}_4:\text{C}_2\text{Cl}_2\text{O}$ , m.p.  $149^\circ$ , is produced in a peculiar reaction from a monocyclic pentene derivative, hexachloro-hydroxycyclopentene-carboxylic acid, the decomposition product of hexachloro-diketocyclohexene, by warming with water or sodium acetate solution (*Zincke*, Ann. 367, 1); it can also be obtained from hexachlororesorcinol and from tetrachloro-*o*-cresol (*Zincke*, Ann. 394, 3).

**HYDRINDENE DERIVATIVES.** Hydrindene,  $\text{C}_8\text{H}_8:\text{C}_2\text{H}_6$ , b.p.  $177^\circ$ , is obtained by the reduction of indene with sodium and alcohol, or by catalytic hydrogenation. It is found in coal-tar in the *cumene* fraction, and it can be obtained from that source through its sulphonic acid (*Moschner*, Ber. 33, 737; 34, 157). On heating with hydrogen and finely divided nickel it is reduced to octahydrindene, bicyclononane,  $\text{C}_8\text{H}_{16}$ , b.p.  $164^\circ$ . Substituted hydrindenes are obtained by reduction of the corresponding indenones or indandiones (*Fleischer*, Ann. 422, 231; *Freund*, Ann. 414, 31). A bromohydrindene, m.p.  $125^\circ$ , is obtained from hydrindene and bromine (*Borsche*, Ber. 54, 102). 5-Bromohydrindene, b.p.  $113\text{--}114^\circ$  (16 mm.), is obtained from 5-aminohydrindene (*Borsche*, Ber. 59, 1913). Dichloro- and dibromohydrindene,  $\text{C}_8\text{H}_8:\text{C}_2\text{H}_4\text{Br}_2$ , an oil, and m.p.  $32^\circ$ , respectively, give on warming with water chloro- and bromo-hydroxyhydrindene, m.p.  $129^\circ$  and  $131^\circ$ . These are converted by ammonia in the cold into aminohydroxyhydrindene, m.p.  $133^\circ$ . When this is acted upon by nitrous acid it gives 1,2-dihydroxyhydrindene,  $\text{C}_8\text{H}_8:\text{C}_2\text{H}_2(\text{OH})_2$ , m.p.  $99^\circ$ , which can also be obtained

from indene by the action of permanganate (*Spilker*, Ber. 26, 1539; *Heusler*, Ber. 32, 30).

When hydrindene is nitrated it gives a mixture of 4- and 5-nitrohydrindene. Pure 4-nitrohydrindene, m.p. 40°, b.p. 145–146° (16 mm.), can be obtained by a rather roundabout method from 5-acetyl-4-nitrohydrindene (*Borsche*, Ber. 54, 102; 59, 1909). The sulphonation of hydrindene leads to a mixture of 4- and 5-monosulphonic acids, the latter predominating at higher temperatures (*Borsche*, Ber. 54, 105).

1-Aminohydrindene is obtained by the action of ammonia on 1-chlorohydrindene (*Courtot*, C.r. 178, 493). 2-Aminohydrindene is a colourless oil, b.p. 229°, which is obtained by the Curtius degradation of hydrindene-2-carboxylic acid. The hydrochloride, m.p. 240–241°, causes an increase in blood pressure. 4-Aminohydrindene, m.p. –3°, is obtained by reduction of the nitro-compound (*Goth*, Ber. 61, 1459). 5-Amino-hydrindene, b.p. 146–147° (25 mm.), is obtained by the Beckmann transformation of 5-ethyl-hydrindene-oxime (*Borsche*, Ber. 57, 658). 5-Hydroxy-hydrindene, m.p. 55°, is obtained from the 5-amino-compound. For hydroxyamino-hydrindenes, see *von Braun*, Ber. 55, 3648; *Mills*, J. 1930, 2510.

Hydrindene-2-carboxylic acid,  $C_8H_8(CH_2)_2CH \cdot COOH$ , m.p. 130°, gives indene when its salts are distilled, and is converted into indene-carboxylic acid by bromine. It is oxidised by permanganate to phthalonic acid (p. 440). It is obtained by removing carbon dioxide from hydrindene-2,2-dicarboxylic acid, m.p. 199°, of which the ester can be obtained synthetically from xylene bromide and diethyl malonate (p. 592). By the action of acetoacetic ester on xylene bromide, 2-

acethydrindene-carboxylic ester,  $C_8H_8(CH_2)_2C \begin{array}{l} \swarrow COCH_3 \\ \searrow COOR \end{array}$ , is formed. 1-Methyl-

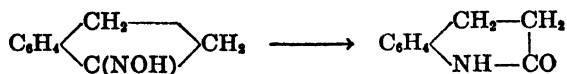
hydrindene-2-carboxylic acid, m.p. 86°, see *Neville*, Proc. 22, 64; J. 89, 383. Hydrindene-5-carboxylic acid, m.p. 178–179°, is obtained from hydrindene, oxalyl chloride, and aluminium chloride at 0° (*von Braun*, Ber. 53, 1159).

Hydrindene-2-methyl-, -ethyl-, and -phenyl ketones are obtained by the distillation of the calcium salt of hydrindenecarboxylic acid with calcium acetate, propionate and benzoate, respectively (*Spilker*, Ber. 26, 1539).

Hydrindene-5-methyl ketone, b.p. 134–135° (11 mm.), is obtained from hydrindene, acetyl chloride and aluminium chloride (*von Braun*, Ber. 53, 1164).

1-Hydrindone, or 1-indanone,  $C_8H_8 \begin{array}{l} \swarrow CH_2 \\ \searrow CO \end{array} CH_2$ , m.p. 41°, b.p. 244°, is ob-

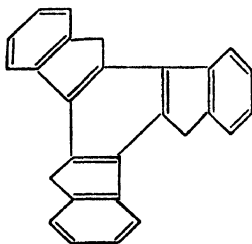
tained by the dry distillation of hydrocinnamic-*o*-carboxylic acid (p. 394), by warming *o*-cyanohydrocinnamic ester with concentrated hydrochloric acid, and from the action of aluminium chloride on  $\beta$ -phenylpropionyl chloride (*Thiele*, Ann. 376, 271). It can also be obtained from hydrocinnamyl chloride and benzene by the action of aluminium chloride (*Aamgat*, Bull. [4], 41, 940), or by oxidation of 1-chloroindane with dichromate (*Courtot*, C.r. 182, 320). The phenylhydrazine melts at 131°. The oxime, m.p. 146°, is converted into 1-aminohydrindene on reduction. This substance boils at 220°, and its hydrochloride is converted almost quantitatively on heating into ammonium chloride and indene. With nitrite, the amino-compound gives 1-hydroxy-hydrindene, m.p. 54° (*Wislicenus*, Ann. 275, 347; *Kipping*, Proc. 15, 172; 16, 54). 1-Hydrindone-oxime is converted into hydrocarbostyryl by phosphorus pentachloride (Beckmann transformation) (*Kipping*, Proc. 1893, 240).



With hydrazine, hydrindone gives hydrindone-azine,  $C_8H_8:N:N:C_8H_8$ , m.p. 165°. With nitrous acid it gives isonitrosohydrindone,  $C_8H_8 \begin{array}{l} \swarrow CH_2 \\ \searrow CO \end{array} C:NOH$ ,

m.p. 210° (decomp.), which gives an osazone, m.p. 229° with phenylhydrazine, which is isomeric with the dihydrazone obtained from 1,3-diketohydrindene, and gives 2-amino-1-hydrindone on reduction (*Gabriel*, Ber. 29, 2605; *Kipping*,

Proc. 1895, 214; J. 71, 238). By the action of concentrated sulphuric acid a Beckmann transformation takes place, and homophthalamidic acid is formed (Peters, Ber. 40, 240). It is very easily decomposed with formaldehyde and hydrochloric acid. From 2-isonitroso-3-methyl-hydrindone, m.p. 130°, 3-methyl-1,2-indandione is formed in this way (von Braun, Ber. 46, 3041). With benzaldehyde (cf. Feuerstein, Ber. 34, 412) 1-hydrindone gives a benzylidene compound,  $C_9H_6O:CHC_6H_5$ , which forms yellow crystals, m.p. 114°. The same compound is formed by the action of concentrated sulphuric acid on  $\alpha$ -benzylcinnamic acid (p. 580). 2 mols. of hydrindone will condense to give anhydrobis-hydrindone,  $C_9H_6O:C_9H_6$ , m.p. 143°. On further condensation the hydrocarbon, truxene, or tribenzylene-benzene,  $C_{27}H_{18}$ , m.p. 365–368°, is formed.



Truxene

This compound is also obtained by the decomposition of decacyclene (Dziewonski, Ber. 46, 2156; Stobbe, Ber. 52, 1023; 60, 457; Bull. Acad. Sci. de Cracovie, 1915, Jan.–March) and by the energetic reduction of truxone (p. 601).

Truxene-quinone, or tribenzoylene-benzene,  $C_{27}H_{12}O_2$ , orange-yellow needles, m.p. above 360°, is obtained by the oxidation of truxene (Liebermann, Ber. 23, 318) and by heating 1,3-diketohydrindene (Kostanecki, Ber. 30, 2143). With

phthalaldehyde 1-hydrindone condenses to give 2,3-benzo-fluorenone,  $\begin{matrix} C_6H_4 \\ | \\ C_{10}H_6 \end{matrix} \rangle Cr$  (p. 683) (Thiele, Ann. 369, 288). When *o*-, *m*-, and *p*-methylhydrocinnamic acids are heated *o*-, *m*-, and *p*-methyl-1-hydrindone are formed. The constitution of these acids has been established by their oxidation to various methylphthalic acids. *Bz*-Chloro-, bromo-, and -iodo-, and -nitrohydrindones behave similarly (Müller, Ber. 25, 2095).

2-Methyl-1-hydrindone, b.p. 168° (11 mm.) (Kipping, Proc. 18, 34), and 2-phenyl-1-hydrindone, m.p. 78°, are obtained from  $\alpha$ -methyl- and  $\alpha$ -phenylhydrocinnamic acids. When an ether solution of 2-phenyl-hydrindone is shaken with caustic soda it is partly converted into 2-phenyl-hydroxy-hydrindone, m.p. 129°, and some ring-fission also takes place with formation of desoxybenzoin-*o*-carboxylic acid,  $C_6H_4(COOH) \cdot CH_2 \cdot COC_6H_5$  (p. 569) (Müller, Ber. 26, 2095). 1-Phenyl-3-hydrindone, m.p. 78°, is obtained from  $\beta, \beta$ -diphenylpropionic acid and sulphuric acid, or from cinnamyl chloride, benzene, and aluminium chloride (Liebermann, Ber. 26, 2128; Kohler, Am. 44, 60).

2,2-Dimethyl-1-hydrindone,  $C_8H_8 \begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CO \end{matrix} \rangle C(CH_3)_2$ , m.p. 45°, is obtained from

$\alpha, \alpha$ -dimethyl- $\beta$ -phenylpropionyl chloride and aluminium chloride, or by methylation of 1-hydrindone with sodamide and methyl iodide. On heating with sodamide in benzene solution it is broken down to the amide of  $\alpha, \alpha$ -dimethyl- $\beta$ -phenylpropionic acid. 2,2-Diethyl-1-hydrindone, m.p. 70, b.p. 138° (13 mm.) (Haller, C.r. 150, 1472). 3,3-Diphenyl-1-hydrindone, m.p. 129–130°, is obtained from  $\beta, \beta, \beta$ -triphenylpropionic acid and concentrated sulphuric acid (Moureu, Bull. [4], 43, 1367).

Tetrachloro-1-hydrindone,  $C_8H_4Cl_4O$ , m.p. 108°, the addition product of chlorine and dichloroindone (p. 596), is readily broken down on warming with alcoholic soda to *o*-trichlorovinylbenzoic acid. Chlorodibromohydrindone-3-carboxylic acid,  $C_8H_3Cl_2Br_2O(COOH)$ , m.p. 171°, obtained from chloroindone-

3-carboxylic acid and bromine, is also readily broken down in the same way to bromochloromethylene-homophthalic acid (p. 610).

**5-Hydroxy-1-hydrindone**, m.p. 183°, and **4-hydroxy-1-hydrindone**, m.p. 111°, are obtained together from  $\alpha$ -bromopropionic acid phenyl ester with aluminium chloride at 140–150°, and are separated by steam distillation (*Auwers*, Ber. 49, 2410). **6-Hydroxy-1-hydrindone**, m.p. 151–153°, see *Ingold*, J. 123, 1469.

The nitration of 1-hydrindone gives a mixture of 4- and 6-nitro-1-hydrindone. **6-Nitro-1-hydrindone**, m.p. 74°, gives **6-amino-1-hydrindone**, m.p. 171°, on reduction (*Ingold*, J. 123, 1469).

**2-Nitro-1-hydrindone**,  $C_8H_5 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CH} \cdot \text{NO}_2$ , sulphur-yellow needles, m.p.

117° (decomp.), is obtained by condensation of phthalaldehyde and nitromethane in the presence of sodium ethylate (*Thiele*, Ann. 377, 15).

**2-Hydrindone**, or 2-indanone,  $C_8H_7 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{CO}$ , m.p. 61°, b.p. 220–225° (de-

comp.), is obtained by the distillation of calcium *o*-phenylenediacetate (p. 593), by warming hydrindene-glycol or its monomethyl ether with sulphuric acid, and by warming 2-bromo-1-hydroxyhydrindene with caustic potash (*Read*, J. 121, 2550). Hydrazone, m.p. 120°. The oxime, m.p. 155°, gives **2-aminohydrindene**, on reduction (*Wislicenus*, Ann. 275, 351). **Di-isonitroso-2-hydrindone**,  $C_8H_4 : [C(NO)]_2CO$ , m.p. 233° (decomp.). Like 1-hydrindone and the diketohydrindenes, 2-hydrindone readily condenses to anhydro-bis-2-hydrindone,  $C_8H_6O : C_8H_8$ , m.p. 170° (*Heuser*, Ber. 32, 28).

**Tetrachloro-2-hydrindone**,  $C_8H_4 : C_2Cl_4O$ , m.p. 98°, is obtained by the action of calcium chloride on tetrachloro-2,3-diketo-tetrahydronaphthalene (p. 644). **Monobromo-, 1,3-dibromo- and tetrabromo-hydrindone**, m.p. 91°, 111°, and 173°, respectively, are obtained by brominating 2-hydrindone in benzene solution. Tetrachloro- and tetrabromo-hydrindone pass into phthalide-carboxylic acid on warming with alkalis (benzilic acid transformation) (*Zincke*, Ann. 334, 346; *Thorpe*, J. 93, 1507).

**2-Acetyl- and 2-benzoyl-1-hydrindone**, m.p. 76° and 98° (*Thiele*, Ann. 347, 112). **1-Hydrindone-2-oxalic acid**, m.p. 212°, is obtained by method of formation 5 (p. 593) (*Thiele*, Ann. 369, 287).

**1,2-Indandione**, m.p. 95–115°, is obtained by the action of formaldehyde and hydrochloric acid on isonitroso-1-hydrindone. In contrast to 1,3-indandione, the compound has a strong yellow colour (*Perkin*, J. 101, 232; *von Braun*, Ber. 46, 3041).

**1,3-Diketohydrindene**, or 1,3-indandione,  $C_8H_4 : (CO)_2CH_2$ , m.p. 130° (decomp.), is obtained from its carboxylic acid (p. 600). For its formation from  $\alpha$ -naphthaquinone by the action of nitrous acid, see p. 629. It forms colourless needles, which dissolve in alkalis with a yellow colour. The H atoms of the methylene group between the two keto-groups has an acidic character. With phenylhydrazine it forms a monohydrazone, m.p. 163°, and a dihydrazone,  $C_8H_4 : (C : NNHC_6H_5)_2 \cdot CH_2$ , m.p. 171°. By the action of phenyl-diazonium chloride the monohydrazone of a triketohydrindene,  $C_8H_4 : (CO)_2C : NNHC_6H_5$ , is obtained. This is also produced by the fission of benzal-diketohydrindene,  $C_8H_4 : (CO)_2C : CHC_6H_5$ , the condensation product of benzaldehyde and diketohydrindene, by phenylhydrazine. **3',4'-Dihydroxy-benzal-diketohydrindene**, m.p. 257°, obtained by condensation of protocatechuic-aldehyde and diketohydrindene, is a substance which dyes with a mordant (*Kostanecki*, Ber. 30, 1185). Weakly basic dyes are also formed with *p*-aminobenzaldehydes. *o*-Amino-benzaldehyde gives

quinolene-phenylene-ketone,  $C_8H_5 \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{CH} \end{array} \text{C}_6H_4$ , m.p. 175° (*Noelling*,

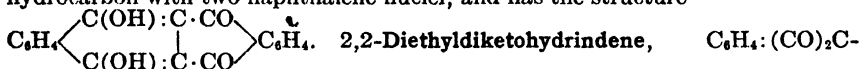
Ber. 34, 2467). For further condensation product of 1,3-indandione with aldehydes, see *Ruhleescu*, Bull. [4], 37, 1069. Substituted 1,3-indandiones can be obtained from alkyl-phenols, homologous malonyl chlorides and aluminium chloride in nitrobenzene. Some of them are good antiseptics. Indandione condenses with ethyl orthoformate to give the compounds:  $C_8H_4 : (CO)_2C : CHOH$  and  $C_8H_4 : (CO)_2C : CH \cdot CH(CO)_2 \cdot C_6H_4$ . The latter gives dibenzoylene-



pyridine,  $\text{CO}-\text{C}(\text{CH}_3):\text{CH}:\text{C}(\text{CH}_3)-\text{CO}$ , with ammonia (*Errera, Gazz. 35, II, 417*).

With ethoxy-methylene-acetoacetic ester indandione combines to give *indandione-methylene-acetoacetic ester*,  $\text{C}_6\text{H}_4(\text{CO})_2\text{CH}:\text{CH}:\text{C}(\text{COCH}_3)\text{COOC}_2\text{H}_5$ , m.p. 118°, which condenses with concentrated alkali to give 3-hydroxy-fluorenone-2-carboxylic acid (p. 683) (*La Spada, Gazz. 35, II, 539*).

**2-Methyl-diketohydrindene**,  $\text{C}_8\text{H}_6:(\text{CO})_2\text{CHCH}_3$ , m.p. 85°, is obtained from its carboxylic acid, and by the transposition of ethylidene-phthalide (pp. 482, 592). Its sodium compound reacts with methyl iodide to give **2,2-dimethyl-diketohydrindene**,  $\text{C}_8\text{H}_6:(\text{CO})_2\text{C}(\text{CH}_3)_2$ , which has also been obtained from the disodium salt of diketohydrindene-carboxylic acid and methyl iodide. **2-Phenyl-diketohydrindene**, m.p. 145°, is obtained from benzalphthalide. Isethine-diphthalyl, m.p. above 350°, obtained by the isomerisation of ethine-diphthalyl (p. 587) with sodium ethylate, forms violet-coloured needles. It was formerly regarded as *bis*-diketohydrindene. It is derived from naphthalene,  $\text{C}_{10}\text{H}_{12}$ , a hydrocarbon with two naphthalene nuclei, and has the structure



( $\text{C}_2\text{H}_5$ )<sub>2</sub>, b.p. 143–156° (10 mm.), oxime, m.p. 143°, is obtained from benzene, diethyl-malonyl chloride and aluminium chloride (*Freund, Ann. 373, 291; 402, 51*). For the application of these methods to the preparation of substituted indandiones naphthindandiones, and acenaphthindandiones, see *Freund, Ann. 399, 182; 402, 51; 409, 268; Fleischer, Ann. 422, 231*.

**2-Dichloro-diketohydrindene**,  $\text{C}_8\text{H}_6:(\text{CO})_2\text{CCl}_2$ , m.p. 125°, is obtained by the action of chlorine on 1-hydroxychlorindone (p. 596). It is broken down into phthalic acid by dilute caustic soda (*Zincke, Ber. 21, 491, 2380*).

**2-Bromo-diketohydrindene**,  $\text{C}_8\text{H}_6:(\text{CO})_2\text{CHBr}$ , is identical with 2-bromo-1-hydroxy-indone (p. 596), and is obtained by bromination and hydrolysis from diketohydrindene-carboxylic ester. On boiling with water it gives  **dibromo-diketohydrindene**,  $\text{C}_8\text{H}_6:(\text{CO})_2\text{CBr}_2$  (for constitution, see *Vorländer, Ann. 322, 244*). With excess of iodine, **2-di-iodo-diketohydrindene**,  $\text{C}_8\text{H}_6:(\text{CO})_2\text{CI}_2$ , is formed (*Liebermann, Ber. 33, 2433; Flatow, Ber. 34, 2145*).

**Diketohydrindene-carboxylic ester**,  $\text{C}_8\text{H}_6:(\text{CO})_2\text{CH} \cdot \text{COOR}$ , m.p. 75–78°, is obtained by the action of sodium ethylate on ethyl phthalate and ethyl acetate. Like the corresponding acid, which can be obtained by isomerisation of phthalyl-acetic acid (*Gabriel, Ber. 26, 954*), it is readily converted into diketohydrindene. **2-Methyl-diketohydrindene-carboxylic ester**,  $\text{C}_8\text{H}_6(\text{CO})_2\text{C}(\text{CH}_3)\text{COOR}$ , is obtained from ethyl phthalate and ethyl propionate. Further derivatives of diketohydrindene, see *Ephraim, Ber. 31, 2084*. **Diketohydrindene aldehyde**,  $\text{C}_8\text{H}_6:(\text{CO})_2\text{CH} \cdot \text{CHO}$ , m.p. 139°, see *Felix, Mo. 31, 62*.

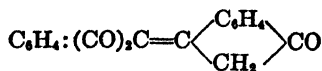
**2-Acetyl- and 2-benzoyl-diketohydrindene**,  $\text{C}_8\text{H}_6:(\text{CO})_2\text{CH} \cdot \text{COR}$ , m.p. 110° and 108°, are obtained from ethyl phthalate and acetone or acetophenone, respectively. They appear to be very readily broken down by alkalis (*Schwerin, Ber. 27, 104*). As shown by their behaviour on ozonisation, the CO-group of the acyl radical readily goes over to the enol form.

**1,2,3-Indane-trione-hydrate**, or ninhydrin, m.p. 239–240° (decomp.), is obtained from 1- or 2-indanone, and from 1,3-indandione by condensation with *p*-nitrosodimethylaniline, and subsequent decomposition with dilute sulphuric acid, and also by oxidation of 1,3-indandione with selenium dioxide (*Teeters, Am. 55, 3026*). It is colourless, but colours the skin red. With hydrogen sulphide

it is converted into **hydrindantin**,  $\text{C}_8\text{H}_6 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}(\text{OH})-\text{O}-\text{CH} \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}_6\text{H}_4$  (a

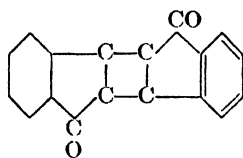
reaction corresponding to the conversion of alloxan into alloxantin). It is used as a reagent for  $\alpha$ -amino-acids, with which it gives a blue colouration (*Ruhemann, J. 97, 1438; 99, 792*).

**Bi-indone** decomposes at 206–208°:

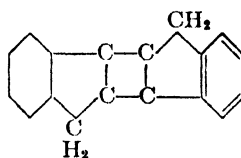


This compound is obtained by warming 1,3-indandione by itself, or by boiling it with water. It gives highly coloured metallic compounds, and gives blue dyes when heated with aromatic amines, water being eliminated. These resemble coerulignon (p. 503) (*Liebermann*, Ber. 30, 3137). Phenylhydrazine decomposes it into two molecules of diketohydrindene-diphenylhydrazone (*Wislicenus*, Ann. 277, 362; *Hoyer*, Ber. 34, 3269). Bi-indone may condense still further to high-molecular substances (*Wislicenus*, Ber. 31, 2935; *Liebermann*, Ber. 33, 2433).

**Iso-bi-indone**,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CH} = \text{C} \begin{array}{c} \diagup \text{CH} \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{CO}$ , a yellow substance, m.p. 330°, is green in solution. It is formed as a byproduct with bi-indone in the treatment of indandione-carboxylic ester with boiling dilute sulphuric acid. It can also be prepared from bi-indone by boiling in benzene solution in the presence of potassium carbonate (*Fischer*, Ann. 489, 97; *Wanag*, C. 1932, I, 1894). A dimeric indone, **truxone**,  $\text{C}_{18}\text{H}_{12}\text{O}_2$ , m.p. 182°, is obtained by dehydrating truxillic acid (*Stoermer*, Ber. 52, 1260; *Stobbe*, Ber. 60, 460, 473). On reduction with hydriodic acid and phosphorus it is broken down and repolymerises to **truxene** (p. 598) (*Liebermann*, Ber. 22, 786). The parent hydrocarbon of truxone is **truxane**,  $\text{C}_{18}\text{H}_{16}$ , m.p. 116°, obtained by the Clemmensen reduction of truxone (*Stobbe*, Ber. 60, 460):

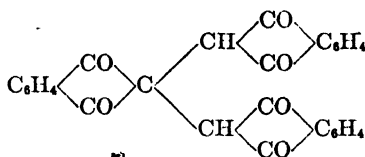


Truxone



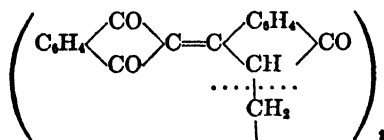
Truxane

*tris*-Diketohydrindene,

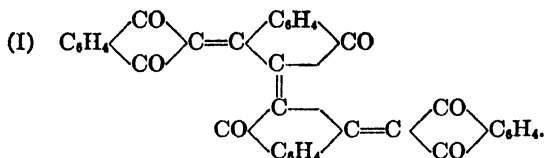


m.p. 266°, is formed by the action of iodine on sodio-diketo-hydrindene-carboxylic ester. With excess of iodine 2-diiodo-diketohydrindene,  $\text{C}_6\text{H}_4(\text{CO})_2\text{Cl}_2$ , is formed (*Liebermann*, Ber. 33, 2434; *Flatow*, Ber. 34, 2145). *tris*-Diketohydrindene forms a red di-potassium salt.

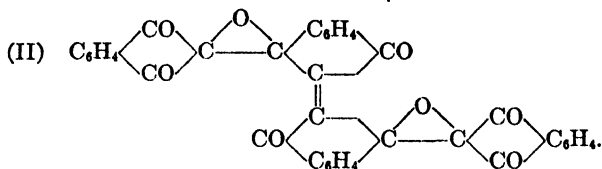
**2,2'-Methylene-bis-indandione**,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_4$ , decomposes at 204–205°. It is produced from 1,3-indandione by the action of formaldehyde in alkaline solution. With acetaldehyde the corresponding **ethylene-bis-indandione**, m.p. 216–218°, is formed. It is possible for bi-indone to condense with aldehydes at the methylene group to give *bis*-bi-indones. Thus, with formaldehyde, methylene *bis*-bi-indone is formed, m.p. 239° (*Radulescu*, Bull. [4], 37, 1187; *Ionescu*, C. 1927, II, 71; Ber. 60, 1228; *Ionescu*, Bull. [4], 45, 428; 51, 1109, 1620):



By the oxidation of indandione-1,3 in non-aqueous solvent with metallic oxides, *trans*-*bis*-bi-indonylene (I) is formed:

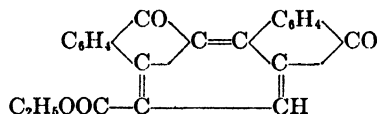


It melts at 340° (decomp.) and is blackish-violet in colour. It is easily further oxidised to *trans*-dioxy-*bis*-bi-indonylene (yellow needles) (II):

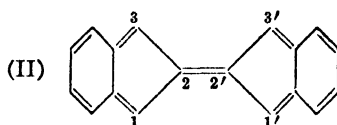
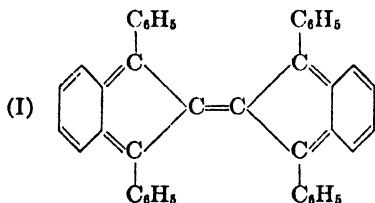


For further oxidation and transformation products, see *Wanag*, *Ann.* 494, 107; and *C.* 1932, I, 1894.

A complex ring system known as **fluoracene** is derived from bi-indone. A derivative of this substance is formed by the condensation of bi-indone with  $\beta$ -iodo-propionic ester. It is **carbethoxy-diketo-*o*-trans-fluoracene**, m.p. 206–207° (*Radulescu*, *C.* 1924, I, 225):

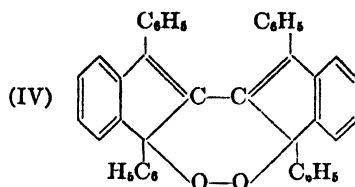
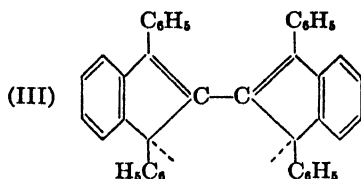


The hydrocarbon **rubrene** (I), or tetraphenyl-rubrene, m.p. 331°, may be regarded as a derivative of bi-indene:



It forms red crystals and is obtained from phenyl-ethynyl-diphenyl-methyl chloride,  $C_6H_5 \cdot C \equiv C \cdot C(C_6H_5)_2Cl$ , by heating, when hydrogen chloride splits off (*Moureu*, *C.r.* 182, 1440; *Willemart*, *C.r.* 187, 385). For another method of preparation, see *Moureu*, *C.r.* 190, 548. The parent hydrocarbon of rubrene is known as **rubene** (II) (*Dufraisse*, *C.r.* 195, 962). It has not yet been prepared. **Dibromorubrene** melts at 310° (*Dufraisse*, *C.r.* 191, 619).

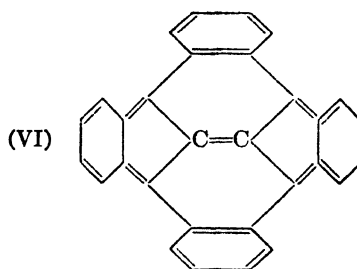
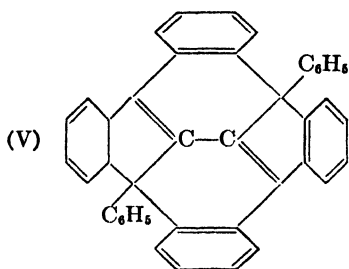
By the action of oxygen in the light, rubrene is converted into a colourless **peroxide**, which forms white needles, m.p. 190°. When heated to 100° it breaks down again into rubrene and oxygen with the emission of light (*Moureu*, *C.r.* 183, 101). In order to explain the formation of a peroxide, rubrene is supposed to be converted into the di-radical form (III) on exposure to light, the peroxide (IV) being derived from this (*Schönberg*, *Ber.* 67, 633). This assumption is not supported by the fact that illuminated and unilluminated solutions of rubrene do not differ in their magnetic properties, and the solid substance itself is diamagnetic, *i.e.*, it is in its normal valency state (*Müller*, *Z. Elektrochem.* 40, 542):



For other oxides of rubrene, see *Dufraisse*, C.r. 188, 1528; 191, 104; 193, 63).

The hydrogenation of rubrene with hydrogen iodide in ether solution leads to the formation of two colourless dihydro-rubrenes, melting at 242° and 225°, respectively (*Dufraisse*, Bull. [4], 51, 74).

**Dehydro-rubrene**,  $C_{42}H_{26}$ , 9,11-diphenyl-9,10,11,12-diphenylene-9,11-dihydronaphthalene (V), is obtained as a by-product in the preparation of rubrene.



Dehydro-rubrene is a colourless hydrocarbon with a violet fluorescence, m.p. 430° (*Dufraisse*, C.r. 194, 183). On treatment with sodium it splits off phenyl-sodium and gives a blue hydrocarbon to which formula VI has been given.

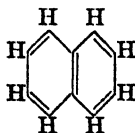
For further rubrene derivatives, see *Dufraisse*, Bull. [4], 53, 782; C.r. 197, 691. For hydrocarbons prepared from rubrene, see *Dufraisse*, C.r. 193, 242, 529.

## 2. NAPHTHALENE GROUP

**Naphthalene**,  $C_{10}H_8$ , was discovered by *Garden* in 1816 among the products obtained by distilling coal-tar. It is very similar chemically to benzene. Like benzene it is formed when various carbon compounds are heated to high temperatures—hence its existence in coal-tar. Naphthalene does not occur in low-temperature carbonisation tar, and this constitutes a characteristic difference between this and ordinary tar. A series of derivatives, analogous to the benzene derivatives, is obtained by replacing the hydrogen atoms of naphthalene. Of the numerous derivatives of naphthalene, only the more important will be dealt with below.

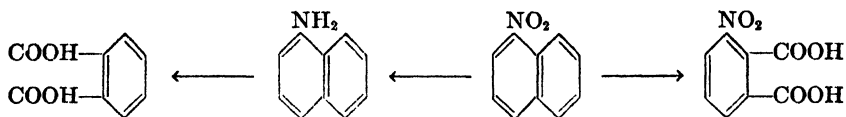
### Constitution of the Naphthalene Nucleus

The reactions of naphthalene are satisfactorily explained by the formula first suggested by *Erlenmeyer* (Ann. 137, 346):

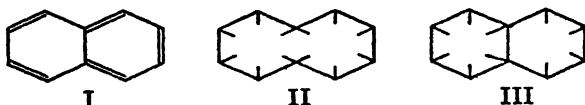


It consists of two benzene nuclei with two carbon atoms in the ortho-position in common. *Graebe* (1866) proved this formula to be correct (Ann. 149, 20).

The oxidation of naphthalene to *o*-phthalic acid shows the presence of a benzene nucleus (p. 384). Further, the oxidation of dichloronaphthaquinone,  $C_6H_4:Cl_2Cl_2O_2$ , also gives *o*-phthalic acid. If, however, dichloronaphthaquinone is converted into tetrachloronaphthalene by phosphorus pentachloride, this compound gives tetrachloro-*o*-phthalic acid on oxidation. In this case, the benzene nucleus which was not attacked in the oxidation of dichloronaphthaquinone, is oxidised. A similar proof, to which reference has already been made (p. 12), is as follows: nitronaphthalene, obtained by nitrating naphthalene, gives nitro-*o*-phthalic acid; but aminonaphthalene, obtained by reducing this nitronaphthalene, gives *o*-phthalic acid:

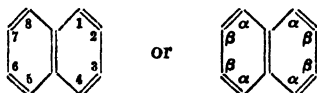


Hence it follows that naphthalene must consist of two symmetrically condensed benzene nuclei. In order to explain the characteristic differences between analogous benzene and naphthalene derivatives, a formula for naphthalene with an asymmetrical distribution of double bonds has been proposed (*Auwers*, Ann. 430, 230). It would be expected from this formula that naphthalene would react with maleic anhydride, but this is not the case. It is also in contradiction to the number of isomers of naphthalene derivatives, which the symmetrical formula satisfactorily explains. For the spectroscopy of naphthalene and its derivatives, see *Auwers*, Ann. 430, 230. For other formulae, such as *Bamberger's* centric formula (II), and the *Armstrong* formula (III), see *Bamberger*, Ann. 257, 1; J. pr. [2], 42, 188; *Ciamician*, Atti. R. Accad. Lincei 1891, I, 378; *Armstrong*, Proc. 1890, 101; *Thiele*, Ann. 306, 136.



For the naphthalene formula in the light of modern views on the benzene problem, see *W. Huckel*, Theoretische Grundlagen der organische Chemie, 2nd ed., 1934, Vol. I.

**ISOMERISM OF NAPHTHALENE DERIVATIVES.** The number of isomers predicted by the accepted naphthalene formula agrees with those actually obtainable. The substituents are named according to the diagram below:\*



The replacement of a hydrogen atom in naphthalene can give rise to two isomeric mono-derivatives, called  $\alpha$ - and  $\beta$ -derivatives, according as the substituent is

adjacent to the group , or is separated from it by a CH group. The

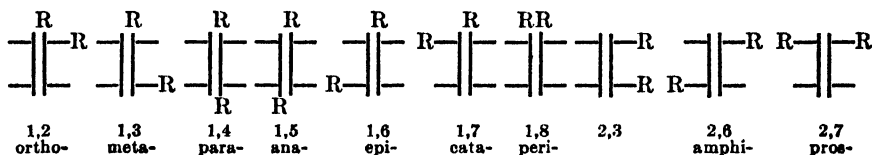
1,4,5,8( $\alpha$ ) positions on the one hand, and the 2,3,6,7( $\beta$ ) positions on the other, are equivalent. *Liebermann* (Ann. 183, 254) and *Allerberg* (Ber. 9, 1736) proved

\* In this translation, the derivatives of naphthalene are named by the number method, except in a few cases.

the equivalence of the four  $\alpha$ -positions. The method used is similar to that followed in demonstrating the equivalence of the hydrogen atoms in benzene. See also *Noelting*, *Rev. gen. des Sciences pures et appl.* 32, 400 (C. 1921, III, 1086).

Whether a substituent is in the  $\alpha$ - or  $\beta$ -position is usually determined by the type of *o*-phthalic acid derivative obtained from it on oxidation. Thus, since  $\alpha$ -nitronaphthalene gives *o*-nitrophthalic acid on oxidation, from which it follows that the nitro-group in the nitronaphthalene must be adjacent to the point of union of the benzene rings in naphthalene. The constitution of  $\alpha$ -hydroxy-naphthalene or  $\alpha$ -naphthol is also evident from its synthesis from phenyl-isocrotonic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$  (p. 469). In addition, only  $\alpha$ -derivatives of naphthalene can be converted into quinones analogous to *p*-benzoquinone, as these are the only ones that have a free H atom in the para position to the substituent. This also gives rise to other peculiarities in the behaviour of naphthalene derivatives, such as the power of the naphthols and naphthylamines to combine with diazo-compounds, *etc.* (p. 618).

There are ten isomeric forms of di-substitution products of naphthalene when the substituents are similar. They are designated by numbers or prefixes (Ber. 26, R 533):



In this diagram the double hexagon of naphthalene is represented by two parallel lines as in the case of benzene (p. 10). If the two substituents are different, the number of isomers is increased to fourteen.

For the calculation of the number of possible isomers of naphthalene derivatives, see *Kauffmann*, *Ber.* 33, 2131.

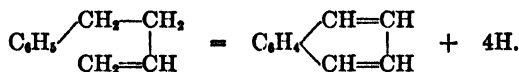
The position of the substituents in di-derivatives can often be determined by oxidation. In this way it is possible to decide whether the two substituents are in the same nucleus (*isonuclear*) or in different nuclei (*heteronuclear*). Isonuclear substitution products with adjacent substituents show in general the same reactions as the ortho-derivatives of benzene, and they form similar condensation products (pp. 108, 205, 214, 220). However, a difference appears to exist between positions such as 1,2 and 2,3. Thus, only those amino-naphthalenes can form naphthaquinoline rings where the pyridine nucleus can attach itself to 1,2-carbon atoms. The reactions of the 1,8- or *peri*-derivatives are also remarkable. Like the *o*-derivatives of benzene and naphthalene, they enter into a number of reactions resulting in formation of heterocyclic rings.

### Formation of the Naphthalene Ring

Naphthalene is formed by pyrogenic condensation from a series of carbon compounds, such as ethylene, acetylene, ether, *etc.* Methods of building up the naphthalene nucleus from compounds in which one benzene nucleus already exists, are more important:

1. A mixture of benzene and acetylene passed through a red-hot tube gives naphthalene (*Berthelot*, *Bull.* [2], 7, 306).

2. Naphthalene is formed when the vapour of phenyl-butylene,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , or its dibromide, is passed over red-hot lime:

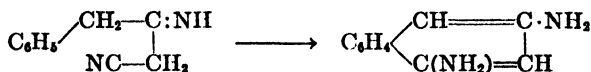


Similar reactions are the formation of phenyl-dihydro-naphthoic acid from dibenzalpropionic acid (p. 584) with a mixture of acetic and sulphuric acids; the formation of phenylbromo-tetrahydro-naphthoic acid from benzylphenyl-iso-



puric acid, and styryl-pyruvic acid,  $\text{C}_6\text{H}_5\text{CH}=\text{CH}\cdot\text{CO}(\text{COOH})\cdot\text{CH}_2$ , obtained by its decomposition, give 1-naphthoic acid (*Erlenmeyer*, Ber. 35, 384).

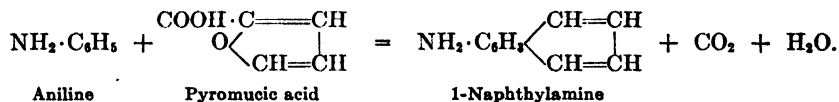
7.  $\gamma$ -Phenyl- $\beta$ -iminobutyro-nitrile condenses under the action of concentrated sulphuric acid to 1,3-diamino-naphthalene (*Best*, Proc. 24, 283; J. 95, 8):



In a similar way,  $\gamma$ -phenyl- $\gamma$ -imino- $\alpha$ -cyanobutyric ester,  $\text{C}_6\text{H}_5\text{C}(\text{:NH})\text{CH}_2\text{NC}\cdot\text{CH}\cdot\text{COOR}$ , gives 1,4-diamino-naphthalene-2-carboxylic ester;

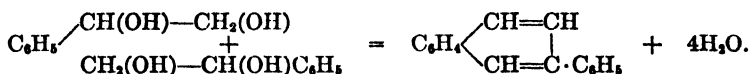
while the iminonitriles,  $\text{C}_6\text{H}_5\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{CH}_2\text{C}_6\text{H}_5$  and  $\text{C}_6\text{H}_5\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{COOR}$  formed by the condensation of *o*-tolunitrile with benzyl cyanide or ethyl cyanoacetate, give 1,3-diamino-2-phenyl-naphthalene, and 1,3-diamino-naphthalene-2-carboxylic ester, respectively (*Atkinson*, Proc. 22, 281; J. 89, 1906; Proc. 23, 76; J. 91, 578; Proc. 23, 316; J. 91, 1687; *Thorpe*, Proc. 23, 151; J. 91, 1004).

8. When aniline is heated with pyromucic acid and zinc chloride to  $300^\circ$ , 1-naphthylamine is formed (*Canzoneri*, Gazz. 18, 486):



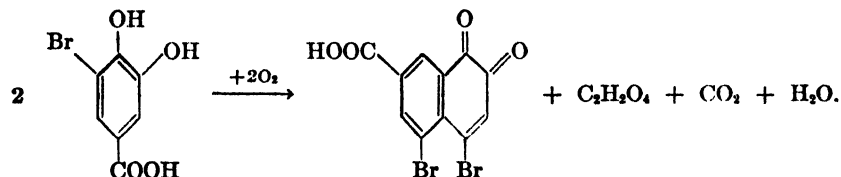
Similarly 1-naphthylamine is formed when aniline hydrochloride is heated with mannitol under pressure.

9. Two molecules of phenyl-glycol condense to give 2-phenyl-naphthalene in the presence of dilute sulphuric acid (*Zincke*, Ann. 240, 137):



Phenylacetaldehyde is an intermediate product. It is formed from one molecule of the glycol by splitting off water, and transformation of the enol- into the tautomeric keto-form.

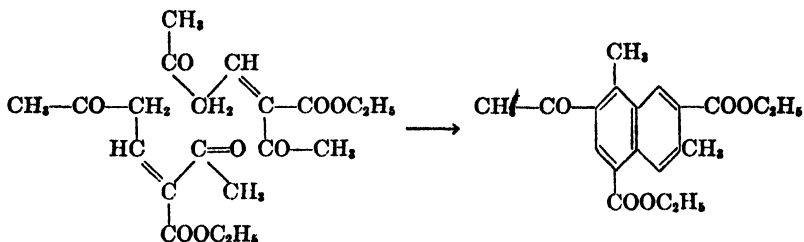
10. The formation of a naphthalene derivative by the oxidation of 5-bromo-protocatechuic acid with nitric acid is peculiar. Dibromo-1,2-naphthaquinone-carboxylic acid is formed (*Zincke*, Ann. 293, 120):



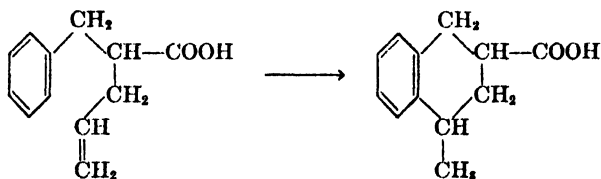
11. Naphthalene derivatives can be obtained by extending the indene ring. Thus, oxindene-carboxylic ester gives 1-hydroxy-4-methoxynaphthalene-2-carboxylic ester with diazomethane (*Hantzsch*, Ber. 63, 566). For ring extension, see further *Radulescu*, Ber. 60, 186.

12. Condensation of  $\alpha,\gamma$ -diacetocrotonic ester with sodium gives aceto-1,6-dimethylnaphthalene-dicarboxylic ester, which can easily be converted into 1,6-dimethylnaphthalene (*Feist*, Ber. 60, 199):



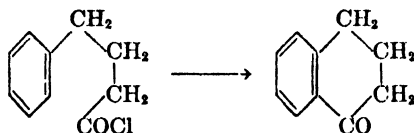


13. Another general process for the synthesis of naphthalene derivatives consists in the cyclisation of benzyl-allyl-acetic acid, which leads to tetrahydromethylnaphthalene-carboxylic acid. By dehydrogenation with selenium or sulphur, methylnaphthalene-carboxylic acid is obtained:



(Darzens, C.r. 183, 748; 194, 2056).

14. By ring closure of phenyl-butyl chloride by means of aluminium chloride, keto-tetrahydro-naphthalene is formed. This can be converted into naphthalene by Clemmensen reduction and dehydrogenation with selenium (Heilbron, J. 1930, 2537; Wilkinson, J. 1931, 1333; Ruzicku, Helv. 15, 140):



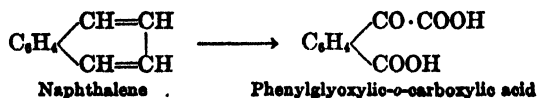
Methods 13 and 14 have been used particularly in the preparation of alkylated naphthalenes.

For further syntheses of naphthalene derivatives, see Weiss, Ber. 58, 1043; Darzens, C.r. 190, 1305.

### Fission of the Naphthalene Ring

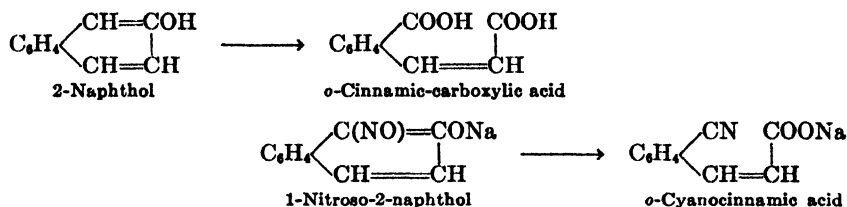
Naphthalene and most naphthalene derivatives are converted into phthalic acid or substituted phthalic acids by energetic oxidation, one of the benzene rings being destroyed. The oxidation is made easier by introducing an amino-group into the benzene ring to be destroyed (*cf.* p. 604). Naphthols and naphthol derivatives are broken down to phthalic acid and benzoic acid by heating with alkali and oxidising metallic oxides (Ger. Pat. 140,999). In many cases it has been possible, by moderating the oxidation, to isolate the intermediate products of the reaction, and sometimes the primary products in the decomposition of the ring.

1. *Decomposition by gentle oxidation.* (a) When oxidised with permanganate, naphthalene gives phenylglyoxylic-*o*-carboxylic acid (p. 440), in addition to phthalic acid (Ger. Pat. 79,693; Graebe, Ber. 31, 369; Daly, J. Phys. Chem. 11, 93):

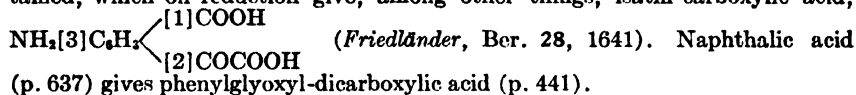


The oxidative fission of naphthalene to phthalic acid by the action of concentrated sulphuric acid and mercuric sulphate (Ger. Pat. 91,202) and, more recently, the direct oxidation of naphthalene by atmospheric oxygen in the presence of certain catalysts (molybdenum oxide, vanadic acid, *etc.*) are of technical importance. In fact, the last-mentioned process is the most important synthesis of phthalic acid (Wohl, Ger. Pat. 379,822).

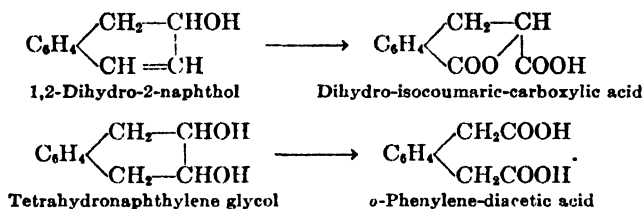
(b) Oxidation of 1- and 2-naphthols with alkaline permanganate gives phenylglyoxyl-*o*-carboxylic acid. By very careful oxidation, 2-naphthol gives, among other substances, *o*-cinnamic-carboxylic acid (p. 483) (Ehrlich, Mo. 10, 115). Beside this reaction we may place the decomposition of sodio-1-nitroso-2-naphthol to *o*-cyanocinnamic acid, by heating to 250° (Ger. Pat. 116,123):



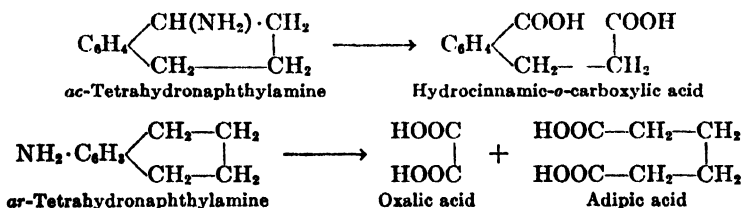
When 1-nitronaphthalene is oxidised with permanganate substances are obtained, which on reduction give, among other things, isatin-carboxylic acid,



(c) Hydrogenated naphthalene derivatives are particularly readily decomposed (p. 641). 1,2-Dihydro-2-naphthol gives dihydro-isocoumaric-carboxylic acid when oxidised with permanganate, and tetrahydronaphthalene glycol gives *o*-phenylene-diacetic acid (p. 395) with dichromate in the cold (Banberger, Ber. 26, 1833):

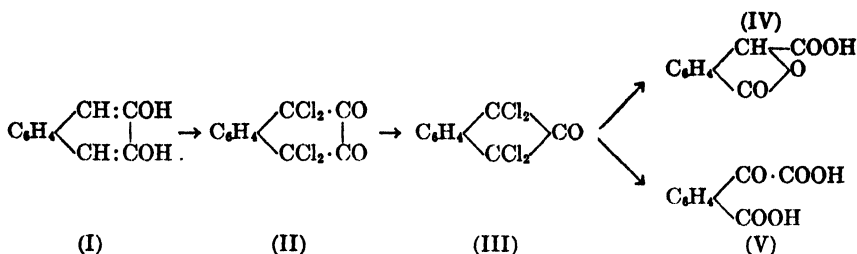


*ac*-Tetrahydronaphthylamine gives hydrocinnamic-*o*-carboxylic acid with permanganate. *ar*-Tetrahydronaphthylamine on the other hand gives adipic and oxalic acids, by oxidation of the benzene nucleus containing the amino-group (Ber. 22, 767):

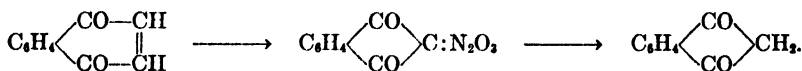


2. *Fission by simultaneous chlorination and oxidation.* The ring-decompositions produced by the action of chlorine or hypochlorous acid on 1,2-naphthoquinone and its derivatives are very numerous. They proceed in the same way as the corresponding reactions with the benzene ring. Two groups may be dis-

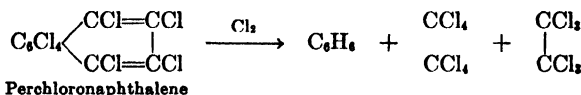




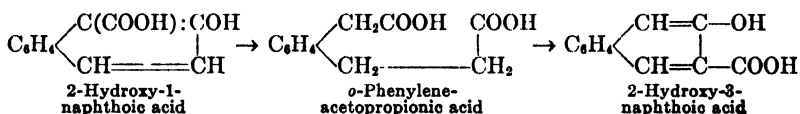
3. The conversion of the naphthalene nucleus into the indene nucleus can also be carried out by the action of liquid nitrous acid on *p*-naphthaquinone. A diketohydrindene-nitrosite is first formed, which, on careful treatment with water gives 1,3-diketohydrindene (p. 599) (*Schmidt*, Ber. 33, 543):



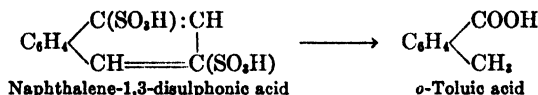
4. Perchloronaphthalene, when heated with antimony chloride to 280–300°, breaks down into perchlorobenzene, tetrachloromethane and hexachloromethane (*Ruoff*, Ber. 9, 1486):



5. *Decomposition by reduction in alkaline solution.* A ring decomposition analogous to that of salicylic acid (p. 32), is that undergone by 2,1- and 2,3-hydroxynaphthoic acids (p. 636) by the action of sodium on their alcoholic solutions (*Einhorn*, Ann. 286, 268):



6. A peculiar decomposition is that given by naphthalene-disulphonic acids, and naphthylamine- and naphthol-sulphonic acids, containing substituents in the 1,3-positions. When fused with potash they give *o*-toluic acid:



In a similar way, 1,3,6- and 1,3,8-naphthalene-trisulphonic acids give *m*-cresol when fused with potash (Ger. Pats. 79,028 and 112,176; *Zincke*, Ann. 350, 253).

### (a) Naphthalene and Its Homologues

**NAPHTHALENE**, C<sub>10</sub>H<sub>8</sub>, m.p. 81°, b.p. 218°, occurs in coal-tar, and is obtained by crystallisation from the fraction distilling at 180–250°. It is purified by fusion with a little concentrated sulphuric acid, separating the resinified acids, and distilling, or (less frequently) subliming the residue. Naphthalene is also found in some essential oils (*Soden*, Pharm. Ztg. 47, 779). It is difficultly soluble in cold alcohol and ligroin, but dissolves readily in ether and hot alcohol. It crystal-

lises and sublimes in colourless, lustrous leaflets. Naphthalene is characterised by its volatility (also with steam) and possesses a characteristic odour. It forms a crystalline molecular compound with picric acid,  $C_{10}H_8 \cdot C_6H_3(NO_2)_3OH$ , m.p.  $149^\circ$  (*Fritzsche*, J. 1857, 456). *m*- and *p*-Dinitrobenzene, trinitrobenzene, trinitrotoluene, etc., form similar molecular compounds.

Naphthalene has a considerable use in industry, particularly in the dyestuff industry. It is used on the one hand for the preparation of phthalic acid, and on the other for manufacturing numerous derivatives (naphthalene-sulphonic acids, naphthylamines, naphthols, naphthylamine sulphonic acids, naphthol sulphonic acids, etc.) which are used in the production of azo-dyes. On account of its strong antiseptic properties it is used as an insecticide.

Naphthalene shows the characteristic properties of the aromatic ring, though to a smaller degree than benzene. Thus, it is chlorinated, nitrated, and sulphonated by halogens, nitric acid, and sulphuric acid, respectively. It differs from benzene in the ease with which it is hydrogenated with formation of di-, tetra-, and higher hydrogenated derivatives. These hydroaromatic compounds, and their importance in connection with stereochemistry, are dealt with in Vol. II. Naphthalene forms addition products with gaseous chlorine even more readily than benzene, e.g., naphthalene dichloride,  $C_{10}H_8Cl_2$ , and naphthalene tetrachloride,  $C_{10}H_6Cl_4$ . For oxidation products of naphthalene see p. 604.

**HOMOLOGUES OF NAPHTHALENE.** Methylated naphthalenes are found in coal-tar and in mineral oil (Ger. Pat. 95,579; *Libavin*, J. Russ. Phys.-Chem. Soc. 31, 358). Alkylated naphthalenes are obtained from bromo-naphthalenes by the action of alkyl halides and sodium, from naphthalene by the action of alkyl iodides or bromides, and aluminium chloride, and by the reduction of acyl-naphthalenes with hydrogen and finely divided nickel at  $180^\circ$ , or by hydriodic acid and red phosphorus (*Darzens*, C.r. 146, 933; *Bargellini*, Atti. Accad. Lincei Roma [5], 17, II, 26). They have also been obtained by the action of lithium and dimethyl sulphate on halogeno-naphthalenes (*Vesely*, Coll. Trav. Tchechoslov. 4, 139). For some further syntheses, see p. 608.

|                                     | M.p.             | B.p.                                  |
|-------------------------------------|------------------|---------------------------------------|
| 1-Methylnaphthalene.....            | $-20^\circ$      | $240-243^\circ$                       |
| 2-Methylnaphthalene.....            | $+32.5^\circ$    | $241-242^\circ$                       |
| 1,2-Dimethylnaphthalene.....        | Liquid           | $148-149^\circ$ (18 mm.) <sup>b</sup> |
| 1,4-Dimethylnaphthalene.....        | Liquid           | $262-264^\circ$                       |
| 1,6-Dimethylnaphthalene.....        | Liquid           | $262-263^\circ$ <sup>d</sup>          |
| 2,3-Dimethylnaphthalene.....        | $104^\circ$      | $260-265^\circ$ <sup>b, d</sup>       |
| 2,6-Dimethylnaphthalene.....        | $110-111^\circ$  | $261-262^\circ$ <sup>d</sup>          |
| 2,7-Dimethylnaphthalene.....        | $96-97^\circ$    | $262^\circ$ <sup>d</sup>              |
| 1-Ethylnaphthalene.....             | Liquid           | $258^\circ$                           |
| 2-Ethylnaphthalene.....             | $-19^\circ$      | $251^\circ$                           |
| 1- <i>n</i> -Propylnaphthalene..... | Liquid           | $274^\circ$                           |
| 2- <i>n</i> -Propylnaphthalene..... | Liquid           | $278^\circ$                           |
| 1- <i>n</i> -Butylnaphthalene.....  | Liquid           | $282^\circ$                           |
| 2- <i>n</i> -Butylnaphthalene.....  | Liquid           | $284^\circ$                           |
| 1-Isobutylnaphthalene.....          | Liquid           | $137^\circ$ (11 mm.)                  |
| 2-Isobutylnaphthalene.....          | Liquid           | $112^\circ$ (6 mm.)                   |
| 1-Phenylnaphthalene.....            | About $45^\circ$ | $325^\circ$                           |
| 2-Phenylnaphthalene.....            | $102^\circ$      | $347^\circ$                           |

<sup>a</sup> *Wendt*, J. pr. [2], 46, 317. <sup>b</sup> *Schroeter*, Ber. 51, 1587. <sup>c</sup> *Cannizzaro*, Atti. R. Accad. Lincei, 1895, I, 287. <sup>d</sup> *Weissgerber*, Ber. 52, 346. <sup>e</sup> *Weissgerber*, Ber. 52, 370. *Vesely*, Coll. Trav. Tchechoslov. 3, 440.

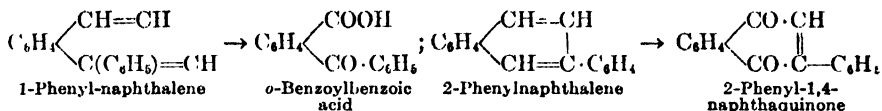
2,3-Dimethylnaphthalene is identical with guaiane, obtained by the dry distillation of guaiac resin. 1,2,7-Trimethylnaphthalene or *sapotalin* has been obtained by dehydrogenation of a series of saponins by selenium (*Ruzicka*, Z. physiol. Chem. 184, 69). For the synthesis of *sapotalin*, see *Ruzicka*, Helv. 15, 140; *Spath*, Mo. 60, 117. Two further homologues of naphthalene have been ob-

tained by dehydrogenation of the sesquiterpenes, **cadaline**, 2,5-dimethyl-8-isopropylnaphthalene, and **eudaline**, 3-isopropyl-5-methylnaphthalene. Both have been synthesised (*Ruzicka*, *Helv.* 5, 923; *Darzens*, *C.r.* 194, 2056; *Cook*, *J.* 1933, 22).

**1,2,5-Trimethylnaphthalene**, b.p. 147–148° (11 mm.), picrate, m.p. 137–138°; **1,3,5-trimethylnaphthalene**, m.p. 47°, picrate, m.p. 141–142°. For further trimethylnaphthalenes, see *Heilbron*, *J.* 1930, 2357. For the preparation and constitution of a number of trimethylnaphthalenes, their picrates and styphnates, see *Ruzicka*, *Helv.* 15, 140.

**1,2,5,6-Tetramethylnaphthalene**, m.p. 116°, is obtained by the dehydrogenation of some triterpenes with selenium, together with 2,7-di- and 1,2,7-trimethylnaphthalenes. For the synthesis of this and other tetramethylnaphthalenes, see *Ruzicka*, *Helv.* 16, 314.

1- and 2-Phenylnaphthalenes have been obtained by the action of phenyldiazonium chloride on naphthalene in the presence of aluminium chloride. A nitrophenylnaphthalene, m.p. 129°, has been obtained similarly from sodium-nitrophenyl-nitrosamine and naphthalene (*Kuhling*, *Ber.* 29, 1681; *cf.* p. 125). 2-Phenylnaphthalene is also formed from bromobenzene and naphthalene by passing their vapours through a red-hot tube, by condensation of 2 mols. of phenyl-glycol, and by distillation of 2-phenyl-3-hydroxy-1,4-naphthaquinone with zinc dust (*Schmid*, *Ber.* 26, 1119; *Bamberger*, *Ber.* 29, 1748; *Volhard*, *Ann.* 296, 28). The constitution of the isomeric phenylnaphthalenes can be arrived at from their oxidation products. 1-Phenylnaphthalene gives *o*-benzoylbenzoic acid, but 2-phenylnaphthalene, on the other hand gives 2-phenyl-1,4-naphthaquinone:



**Olefine-naphthalenes.** **1-Vinyl-naphthalene**,  $\text{C}_{10}\text{H}_7 \cdot \text{CH}:\text{CH}_2$ , b.p. 137° (13 mm.), is obtained by the action of acetaldehyde on 1-naphthyl-magnesium bromide. **1-Allyl-naphthalene**,  $\text{C}_{10}\text{H}_7 \cdot \text{CH}_2 \cdot \text{CH}:\text{CH}_2$ , b.p. 266°, is obtained from allyl bromide and 1-naphthyl-magnesium bromide. On warming with alcoholic potash it is converted into the isomeric **1-propenyl-naphthalene**,  $\text{C}_{10}\text{H}_7 \cdot \text{CH}:\text{CHCH}_3$ , b.p. 138° (10 mm.), which can also be obtained from propionic anhydride, 1-naphthaldehyde, and sodium propionate by removing water and carbon dioxide (*Roussel*, *Bull.* [3], 17, 812; *Tiffeneau*, *C.r.* 147, 678). 1- and 2-**Isopropenyl-naphthalene**,  $\text{C}_{10}\text{H}_7 \cdot \text{C}(\text{:CH}_2)\text{CH}_3$ , 1- b.p. 125° (8 mm.), 2- m.p. 45–47°, b.p. 139° (7 mm.), are obtained by the action of 1- and 2-naphthyl-methyl ketones (p. 634) on methyl magnesium iodide. The 2-compound is obtained directly, the 1-compound by the action of acetic anhydride on the 1-naphthyl-dimethyl carbinol first formed (*Grignard*, *Bull.* [3], 25, 497).

### Substitution Products of Naphthalene

With the exception of sulphonation at high temperatures, substitution in the naphthalene nucleus leads to 1- (or  $\alpha$ -) derivatives.

For substitution rules for the introduction of further substituents into the mono-derivatives, see *Vesely*, *Bull.* [4], 33, 955.

**1. HALOGEN DERIVATIVES OF NAPHTHALENE.** Halogen derivatives of naphthalene are produced: 1. By direct substitution of hydrogen atoms by halogens. 2. By the replacement of the  $\text{NH}_2$  groups in aminonaphthalenes with halogens through the diazo-compounds (pp. 50, 123). 3. By replacement of  $\text{OH}$ ,  $\text{SO}_3\text{H}$ , and  $\text{NO}_2$  groups in the corresponding derivatives by heating with phosphorus pentachloride. The last reaction can be used for the

determination of orientation of naphthalene- or naphthol-sulphonic acids.

The strength of the bond linking the halogens, and other substituents, such as  $\text{NO}_2$  and  $\text{SO}_3\text{H}$  to the nucleus is weaker in general than the corresponding bond in benzene derivatives.

**Fluoronaphthalenes**,  $\text{C}_{10}\text{H}_7\text{F}$ . The 1-compound melts at  $-8$  to  $-9^\circ$ , and boils at  $212^\circ$ . The 2-compound melts at  $61^\circ$ , and boils at  $211.5^\circ$  (737 mm.). For other fluoro-derivatives of naphthalene, see *Schiemann*, Ann. 487, 270.

**Chloronaphthalenes**,  $\text{C}_{10}\text{H}_7\text{Cl}$ . 1- b.p.  $263^\circ$ ; 2- m.p.  $56^\circ$ , b.p.  $265^\circ$ . 1-Chloronaphthalene is obtained (1) by chlorination of boiling naphthalene, (2) by the action of alcoholic potash on dichloronaphthalene, (3) by the action of phosphorus pentachloride on naphthalene-1-sulphonic acid, and (4) from 1-naphthylamine. 2-Chloronaphthalene is obtained from 2-naphthylamine, or from 2-naphthol. All ten of the possible dichloronaphthalenes,  $\text{C}_{10}\text{H}_6\text{Cl}_2$ , are known: 1,2- m.p.  $35^\circ$ , b.p.  $281^\circ$ ; 1,3- m.p.  $61^\circ$ , b.p.  $289^\circ$ ; 1,4- m.p.  $68^\circ$ , b.p.  $287^\circ$ ; 1,5- m.p.  $107^\circ$ ; 1,6- m.p.  $48^\circ$ ; 1,7- m.p.  $62^\circ$ , b.p.  $286^\circ$ ; 1,8- m.p.  $83^\circ$ ; 2,3- m.p.  $120^\circ$ ; 2,6- m.p.  $135^\circ$ , b.p.  $285^\circ$ ; 2,7- m.p.  $114^\circ$  (*Cleve*, Ber. 24, 3475; *Armstrong*, Proc. 61, 5; 1890, 71; 1890, 76; *Erdmann*, Ber. 26, R 536). Trichloronaphthalene. There are fourteen isomers; see *Armstrong*, Proc. 1895, 84; 1896, 152.

**Pentachloronaphthalene**,  $\text{C}_{10}\text{H}_2\text{Cl}_5$ , m.p.  $168^\circ$ ; **perchloronaphthalene**,  $\text{C}_{10}\text{Cl}_8$ , m.p.  $203^\circ$ , b.p.  $403^\circ$ .

**Bromonaphthalenes**,  $\text{C}_{10}\text{H}_7\text{Br}$ , 1- m.p.  $5^\circ$ , b.p.  $279^\circ$ ; 2- m.p.  $59^\circ$ , b.p.  $282^\circ$ . The 1-bromo-compound is partially converted into the 2-compound by heating with aluminium chloride. For polybromonaphthalenes, see *Missenden*, Chem. News, 125, 158; *Salkind*, J. Russ. Phys. Chem. Soc. 62, 1021; C. 1932, I, 3059.

**Iodonaphthalenes**,  $\text{C}_{10}\text{H}_7\text{I}$ , 1-compound b.p.  $305^\circ$ , 2-compound m.p.  $54.5^\circ$ . 1-Iodonaphthalene can be obtained by the addition of iodine to a solution of mercury-dinaphthyl in carbon disulphide, and by iodination of naphthalene with sulphur iodide and nitric acid (Ger. Pat. 123,746). **Bromoiodonaphthalenes**, see Ber. 29, 1408. For naphthyl-iodochloride,  $\text{C}_{10}\text{H}_7\text{ICl}$ , **iodosonaphthalenes**,  $\text{C}_{10}\text{H}_7\text{IO}$ , **iodoxynaphthalenes**,  $\text{C}_{10}\text{H}_7\text{IO}_2$ , and **naphthylphenyl-iodonium hydroxide**,  $(\text{C}_{10}\text{H}_7)(\text{C}_6\text{H}_5)\text{I}\cdot\text{OH}$ , see *Willgerodt*, Ber. 29, 1573; 33, 692.

2. **NITRONAPHTHALENES**. 1-Nitronaphthalene,  $\text{C}_{10}\text{H}_7\text{NO}_2$ , m.p.  $61^\circ$ , b.p.  $304^\circ$ , yellow needles, is obtained by treating naphthalene with nitric acid at ordinary temperatures (*cf. Nageli*, Bull. [3] 21, 786). It gives 1-chloronaphthalene with phosphorus pentachloride, and *o*-nitrophthalic acid by oxidation with chromic acid. For its oxidation by permanganate, see p. 609. 2-Nitronaphthalene, m.p.  $79^\circ$ , is obtained from 2-nitronaphthylamine by replacing the  $\text{NH}_2$  group by hydrogen, or better from 2-naphthyl-diazonium nitrite,  $\text{C}_{10}\text{H}_7\cdot\text{N}_2\cdot\text{NO}_2$ , by the action of cuprous oxide (*Sandmeyer*, Ber. 20, 1494; *Meisenheimer*, Ber. 36, 4157). When warmed with methyl alcoholic potash, 1- and 2-nitronaphthalenes are converted through a series of intermediate stages into 1,4- and 1,2-naphthaquinone monoxime, and 4,1- and 2,1-nitrosonaphthol (*Meisenheimer*, Ann. 355, 299). Various dinitronaphthalenes have been obtained by nitrating naphthalene at higher temperatures. For the separation of the 1,5- and 1,8-compound see *Willgerodt*, Ber. 29, 1243, 1521. The 1,5-compound melts at  $216^\circ$  and the 1,8-compound at  $170^\circ$ . 1,6-Dinitronaphthalene, m.p.  $161^\circ$ , is obtained from dinitro-2-naphthylamine (*Graebe*, Ann. 335, 142). By the action of fuming sulphuric acid in the cold all three of the above-mentioned dinitronaphthalenes are converted into nitro-*p*-nitrosonaphthols (*Graebe*, Ann. 335, 139, 145). On heating 1,5- and 1,8-dinitronaphthalene with fuming sulphuric acid, preferably with the addition of a reducing agent, naphthazarin, or dihydroxynaphthaquinone is formed (p. 630 and Ger. Pat. 76,922). 1,8-Dinitro-naphthalene gives the so-called potassium naphthocyaninate,  $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_2\text{K}$ , on heating. 1,3-Dinitronaphthalene, m.p.  $144^\circ$ , is obtained from amino-dinitronaphthalene by elimination of the  $\text{NH}_2$  group. Various dinitronaphthalenes are obtained by the action of nitric acid on naphthalene at very low temperatures ( $-50^\circ$  to  $-55^\circ$ ) (*Pictet*, C.r. 116, 815). 1,2-Dinitronaphthalene, m.p.  $158^\circ$ , like 1,3-dinitronaphthalene, can be obtained by the dehydrogenation of tetralines nitrated in the aromatic nucleus. 1,4- and 1,7-Dinitronaphthalene, m.p.  $129^\circ$  and  $156^\circ$ , are obtained by

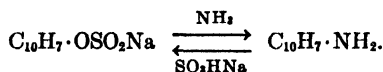
adding diazotised nitronaphthylamines into nitrite solutions containing copper-bronze (*Vesely*, Bull. [4], 33, 319). For other di- and tri-nitronaphthalenes, see *Vesely*, Bull. [4], 33, 942, 952; *Chudozilov*, C. 1929, II, 738. 2,7-Dinitronaphthalene, m.p. 234°, is obtained by decarboxylation of dinitronaphthalic acid (*Rule*, J. 1934, 171). By longer boiling of naphthalene or dinitronaphthalenes with fuming nitric and fuming sulphuric acids tri- and tetranitronaphthalenes are formed (*Will*, Ber. 28, 367). The latter explode violently on heating.

3. NITROSONAPHTHALENES. 1-Nitrosonaphthalene,  $C_{10}H_7NO$ , m.p. 89°, decomp. 134°, is obtained by the action of nitrosyl bromide on mercury-dinaphthyl, or by the oxidation of 1-naphthylhydroxylamine (p. 617) with silver oxide or lead dioxide (*Willstätter*, Ber. 41, 1937). 1,4-Dinitroso-naphthalene, a powder, exploding at 120°, is obtained by oxidation of 1,4-naphthaquinone dioxime with potassium ferricyanide. 1,2-Dinitroso-naphthalene is obtained in a similar way from 1,2-naphthaquinone dioxime. It melts at 127° (*Ilinski*, Ber. 19, 349; *Nietzki*, Ber. 21, 434; *Ponzio*, C. 1906, I, 1700).

4. NAPHTHYLAMINES. (a) The primary amines are obtained by reduction of the nitronaphthalenes. In contrast to the anilines, the naphthylamines are readily obtained by heating the naphthols with ammonia and zinc chloride (p. 621).

They are also obtained by fusing naphthalene-sulphonic acids with sodamide. Naphthalene itself, when heated with sodamide to 220°, in the presence of phenol as an oxidising agent, gives 1-naphthylamine together with 1,5-naphthylene-diamine (*Sachs*, Ber. 39, 3012).

The sulphite compounds of naphthols and derivatives of the naphthols are converted into naphthylamines by treatment with ammonia in aqueous solution even at temperatures about 100°. On the other hand, the amines are reconverted into the sulphite compounds of the naphthols on boiling with solutions of alkali sulphites (*Bucherer*, J. pr. [2], 69, 49):



1-Naphthylamine,  $C_{10}H_7 \cdot NH_2$ , m.p. 50°, b.p. 300°, is obtained by the reduction of 1-nitronaphthalene, or by heating 1-naphthol with zinc chloride-ammonia or calcium chloride-ammonia to 250°. It is obtained synthetically by heating aniline and zinc chloride with pyromucic acid. It crystallises in flat needles, which are particularly beautiful when they separate from aniline solution. It acquires a red colour on exposure to the air. It sublimes readily and has a pungent odour. In general, it behaves in an exactly similar manner to the phenylamines (p. 74). It is reduced by sodium in amyl alcohol solution to tetrahydro-1-naphthylamine (p. 643). The four hydrogen atoms are in the ring not containing the  $NH_2$ . Compounds of this kind are called (aromatic or) *ar*-tetrahydro-1-naphthylamine. It resembles aniline very much, for example, it can be diazotised with nitrous acid. On boiling with chromic acid it is oxidised to 1,4-naphthaquinone. Oxidising agents, e.g., ferric chloride, chromic acid, and silver nitrate, give an azure-blue precipitate of hydroxynaphthylamine,  $C_{10}H_9NO$ , with solutions of salts of naphthylamine (*Schiff*, Ann., 129, 255).

The amino-group in derivatives of 1-naphthylamine can be replaced by the hydroxyl group by treatment with sulphurous acid, followed by alkali (see above, and Ger. Pat. 109,122).



**2-Naphthylamine**, m.p. 112°, b.p. 294°, is obtained from 2-naphthol and zinc chloride-ammonia, or alumina and ammonia at 430–450°. The most convenient method is to heat 2-naphthol with aqueous ammonium sulphite in autoclaves to 100–150°. It is odourless, and gives no colour with ferric chloride, *etc.* It is oxidised by permanganate to phthalic acid. When reduced it gives tetrahydro-2-naphthylamine. In contrast to 1-naphthylamine it is the ring containing the NH<sub>2</sub> group that is hydrogenated, and compounds of this type are called (alicyclic, or) *ac*-tetrahydro-2-naphthylamine. In this compound the amino-group has none of the usual characters of an aromatic amino-group. It is not diazotised by nitrous acid, but forms a very stable nitrite.

(b) *Secondary and tertiary naphthylamines*: Naphthylalkyl-amines are formed in a similar way to the alkyl-anilines by the action of alkyl halides on the naphthylamines, or by heating naphthylamine hydrochlorides with alcohols. They can also be obtained by heating the sulphite compounds of the naphthols with primary and secondary aliphatic amines. The sulphite compounds of 2-naphthol, but not those of 1-naphthol will also react in a similar way with aromatic amines (*Bucherer*, J. pr. [2], 70, 345; 71, 433). 1-Naphthyl-methylamine, C<sub>10</sub>H<sub>7</sub>NHCH<sub>3</sub>, b.p. 293°; 1-naphthyl-ethylamine, b.p. 303°; 2-naphthyl-dimethylamine, C<sub>10</sub>H<sub>7</sub>[2]N(CH<sub>3</sub>)<sub>2</sub>, m.p. 46°, b.p. 305° (*Reychler*, Bull. [3], 27, 970). 2-Naphthyl-methylamine, b.p. 317°, is obtained from 2-naphthol and methylamine at 220° under pressure (*Morgan*, J. 115, 1140). On heating the hydrochlorides of 1- and 2-naphthylamine with aniline and zinc chloride, **phenyl-naphthylamine**, C<sub>10</sub>H<sub>7</sub>·NH·C<sub>6</sub>H<sub>5</sub>, a substance of technical importance, is obtained. 1-Naphthyl-phenylene diamine, see *Merz*, J. pr. [2], 60, 345. When the naphthylamines are heated with zinc chloride or hydrochloric acid to 180–190°, or with 1- and 2-naphthol, various dinaphthylamines are formed. 2,2'-Dinaphthylamine, C<sub>10</sub>H<sub>7</sub>·NH·C<sub>10</sub>H<sub>7</sub>, m.p. 171°, b.p. 471°, occurs as a byproduct in the industrial preparation of 2-naphthylamine. It decomposes when heated with concentrated hydrochloric acid to 150°, into 2-naphthylamine and 2-naphthol. When heated with sulphur, it gives thiodinaphthylamine, NH(C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>S, a compound analogous to thiodiphenylamine (p. 221). By the action of 80% sulphuric acid on 2-naphthylamine in the presence of oxidising agents, naphthidine, (C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>)<sub>2</sub>, is formed, by the linking up of two naphthalene nuclei (*Reverdin*, Chem.-Ztg. 16, 1687) (p. 638).

**Acid derivatives of the naphthylamines** resemble those of the anilines (*cf.* pp. 86–101). 1-Naphthyl-sulphaminic acid, C<sub>10</sub>H<sub>7</sub>·NHSO<sub>2</sub>H, see *de Wildt*, Rec. 23, 173. The reactions of naphthylbenzene-sulphamide, C<sub>10</sub>H<sub>7</sub>·NH·SO<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>, are remarkable. It shows properties similar to those of a naphthol, being soluble in alkalis, and coupling with diazonium salts in the same way as a naphthol (*Witt*, Ber. 27, 2370). For naphthylcarbaminic-chloroethyl-ester, C<sub>10</sub>H<sub>7</sub>·NHCOO·C<sub>2</sub>H<sub>5</sub>Cl, and its decomposition products, see *Otto*, J. pr. [2], 44, 15. For 1-naphthylamine derivatives of succinic, tartaric, and citric acids, see *Bockinger*, Chem.-Ztg. 19, 2080.

**Substituted naphthylamines**. Halogen-substituted naphthylamines are formed by direct substitution, or by the action of ammonia on the substituted naphthols (*cf.* *Reverdin*, Ber. 33, 682).

If acet-1-naphthylamine is nitrated and then hydrolysed, 1,2- and 1,4-nitro-naphthylamine are formed. The 1,4-derivative, m.p. 191°, is converted to 1,4-naphthoquinone by oxidation, to 1-nitronaphthalene by elimination of the amino group, and to 1,4-nitronaphthol by boiling with aqueous alkali (*Lellmann*, Ber. 19, 796; *Orndorff*, Am. Ch. J. 14, 45). The 1,2-derivative, m.p. 144°, yields 2-nitronaphthalene (p. 614) and 2,1-nitronaphthol (p. 623).

If acet-2-naphthylamine is nitrated and hydrolysed, 1-nitro-2-naphthylamine, m.p. 127°, is formed, which gives 1-nitronaphthalene with nitrogen tri-oxide and alcohol. By the addition of 2-naphthylamine nitrate to concentrated sulphuric acid, 5,2- and 8,2-nitronaphthylamine (*Friedländer*, Ber. 25, 2076) are

formed. **2-Nitro-1-naphthylamine**, m.p. 144°, see *Meisenheimer*, Ber. 39, 2541. By partial reduction of dinitro-naphthalenes, the following have been obtained: **1-nitro-3-naphthylamine**, m.p. 95°; **6-nitro-1-naphthylamine**, m.p. 167°, **7-nitro-1-naphthylamine**, and others (*Vesely*, Bull. [4], 33, 942, 952).

**Naphthylene diamines**, or **diaminonaphthalenes** are obtained by the reduction of dinitro- and nitro-amino-naphthalenes, and by decomposition of amino-azonaphthalenes, by heating dihydroxy- and amino-hydroxy-naphthalenes with ammonia, and by fusion of naphthylamines with sodamide (*Lange*, Chem.-Ztg. 12, 856; Ger. Pat. 45,788; *Fischer*, Ber. 26, 188; *Sachs*, Ber. 39, 3012). The *o*-naphthylene diamines, like the *o*-phenylene diamines, show a tendency to enter into condensation reactions, giving rise to heterocyclic derivatives of naphthalene (cf. p. 108). The *o*-naphthylene diamines resemble in many respects the 1,8- or *peri*-compounds (p. 620).

**1,2-Naphthylene diamine**, m.p. 98°, obtained by reduction of 2-nitro-1-naphthylamine or 1,2-naphthaquinone dioxime, and **2,3-naphthylene diamine**, m.p. 191°, obtained by the action of ammonia on 2,3-dihydroxy-naphthalene, give naphtho-azimides with nitrogen trioxide, anhydro-bases with carboxylic acids, quinoxalines with *o*-diketones, etc. (*Fischer*, Ber. 25, 2714; 26, 188; *Friedländer*, Ber. 27, 761). **1,8-(peri)-Naphthylene diamine**, m.p. 67°, obtained from 1,8-dinitro-, or 1,8-dihydroxy-naphthalene reacts in a similar way, giving heterocyclic compounds, but it does not react with the *o*-diketones, such as phenanthraquinone, to give *azines*, as the *o*-diamines do (*Hinsberg*, Ber. 22, 861).

**1,3-Naphthylene diamine**, m.p. 96° (*Friedländer*, Ber. 28, 1953), is obtained synthetically by the action of concentrated sulphuric acid on  $\gamma$ -phenyl- $\beta$ -imino-butyronitrile (p. 607).

**1,3-(*m*)-Naphthylene diamine derivatives** are obtained by the action of amines on naphthylamine sulphonie acids (p. 620), which have the SO<sub>3</sub>H group in the meta-position to NH<sub>2</sub>.

**1,4-Naphthylene diamine**, m.p. 120°, is obtained by the decomposition of 1-aminoazo-naphthalene with zinc and hydrochloric acid, or from 1-nitroamino-naphthalene. With ferric chloride it gives 1,4-naphthaquinone, and with bleaching powder naphthaquinone-dichlorimine.

**1,5-Naphthylene diamine**, m.p. 189°, is obtained from 1-naphthylamine, and **1,6-naphthylene diamine**, m.p. 78°, from 2-naphthylamine by fusion with sodamide (*Sachs*, Ber. 39, 3021).

**1,7-Naphthylene-diamine**, m.p. 117°, see Ber. 25, 2082. **2,6-Naphthylene diamine**, m.p. 222°, see *Jacchia*, Ann. 323, 130. **2,7-Naphthylene diamine**, m.p. 159°, see *Bucherer*, J. pr. [2], 69, 89.

**5. DIAZO- AND AZO-COMPOUNDS OF NAPHTHALENE.** By the action of nitrous acid or sodium nitrite on the salts of naphthylamines, diazo-compounds of naphthalene are formed, which give azo dyes with anilines and phenols, in the same way as the benzene diazonium compounds. In the coupling of diazonium salts with naphthylamines, in the absence of acids, the diazoamino-compounds formed intermediately cannot be isolated. On the other hand, 1- and 2-naphthyl-diazoamino benzene, C<sub>10</sub>H<sub>7</sub>N:N·NHC<sub>6</sub>H<sub>5</sub>, m.p. 84°, and 150° (decomp.), are produced from 1- and 2-naphthyl-diazonium chloride and aniline. The 1-compound can also be obtained by the decomposition of **1-diazo-naphthalenimide** (or 1-naphthyl-azide), C<sub>10</sub>H<sub>7</sub>N<sub>3</sub>, m.p. 12°, with phenyl magnesium bromide, or by the action of phenyl-azide on 1-naphthyl-magnesium bromide (Ber. 40, 2400). **2-Diazonaphthalenimide** (or 2-naphthyl-azide), m.p. 33°, see *Forster*, Proc. 23, 258; J. 91, 1942; *Darapsky*, J. pr. [2], 76, 461. **1-Nitro-2-naphthyl-azide**, C<sub>10</sub>H<sub>6</sub>[1]NO<sub>2</sub>[2]N<sub>3</sub>, m.p. 117°, decomposes on warming with alcohol or glacial acetic acid, giving nitrogen and 1,2-dinitrosonaphthalene (*Forster*, loc. cit.). **2-Naphthyl-nitramine**, C<sub>10</sub>H<sub>7</sub>·NH·NO<sub>2</sub> (see p. 111), gives 2-amino-1-nitronaphthalene on isomerisation (*Bamberger*, Ber. 30, 1262).

**Azonaphthalenes.**—The reduction of the nitronaphthalenes to azoxy- and azo-naphthalenes takes place much less readily than with the nitrobenzenes. 1-Nitronaphthalene gives **1-naphthyl-hydroxylamine**, C<sub>10</sub>H<sub>7</sub>NHOH, m.p. 72° (decomp.), and **1,1'-azoxynaphthalene**, C<sub>10</sub>H<sub>7</sub>N<sub>2</sub>OC<sub>10</sub>H<sub>7</sub>, m.p. 127°, on reduction with zinc dust in neutral solution. By further reduction with zinc dust and alkali, the azoxy-compound gives **1,1'-azonaphthalene**, C<sub>10</sub>H<sub>7</sub>N:NC<sub>10</sub>H<sub>7</sub>, m.p. 190°, red needles, which can also be obtained by deamination of aminoazonaphthalene (*Wacker*, Ann. 321, 61). **2,2'-Azonaphthalene**, C<sub>10</sub>H<sub>7</sub>N:NC<sub>10</sub>H<sub>7</sub>, m.p. 208°, red

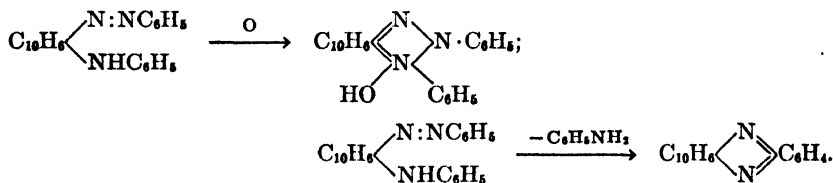
leaflets, is obtained together with dinaphtho-orthodiazine,  $\begin{array}{c} \text{C}_{10}\text{H}_8-\text{N} \\ | \\ \text{C}_{10}\text{H}_8-\text{N} \end{array}$ , and 2,2'-diamino-1,1'-dinaphthyl (see below) by reduction of 2-nitronaphthalene (*Meisenheimer*, Ber. 36, 4153). When oxidised with hydrogen peroxide it gives 2,2'-azoxynaphthalene, m.p. 164°, a yellow substance, which changes into a red isomer, m.p. 162°, on exposure to light (*Cumming*, J. 125, 1108).

**Benzene-azonaphthalene**,  $\text{C}_{10}\text{H}_7 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_5$ , m.p. 65°, *o*-toluene-azonaphthalene,  $\text{C}_{10}\text{H}_7 \cdot \text{N}_2 \cdot \text{C}_7\text{H}_7$ , m.p. 52° (*Nietzki*, Ber. 26, 143). **Naphthyl-azoacetoacetic ester**,  $\text{C}_{10}\text{H}_7 \cdot \text{N}_2 \cdot \text{CH}(\text{COCH}_3)\text{COOR}$  (?), m.p. 94°, obtained from naphthyl diazonium chloride by the action of sodio-acetoacetic-ester, decomposes to naphthylazoacetone when warmed with potash, and naphthyl-azoacetic acid by acid hydrolysis (*Oddo*, Gazz. 21, I, 269).

**Aminoazo-naphthalenes**.—4-Amino-(1,1'-azonaphthalene),  $\text{C}_{10}\text{H}_7[1']\text{N}_2[1]\text{C}_{10}\text{H}_6[4]\text{NH}_2$ , m.p. 175°, is obtained by mixing a solution of 2 molecules of naphthylamine hydrochloride with 1 molecule of sodium nitrite. Diazoamino-naphthalene is first formed,  $\text{C}_{10}\text{H}_7\text{N}_2 \cdot \text{NHC}_{10}\text{H}_7$ , but isomerises (*Michaelis*, Ber. 28, 2198). Aminoazo-naphthylamine is reduced by tin and hydrochloric acid to 1-naphthylamine and 1,4-naphthylene diamine (*Perkin*, Ann. 137, 359). On heating with naphthylamine hydrochloride it is converted into *naphthalene red*, a safranin dye. 2-Amino-(1,2'-azonaphthalene),  $\text{C}_{10}\text{H}_7[2']\text{N}_2[1]\text{C}_{10}\text{H}_6[2]\text{NH}_2$ , m.p. 156°, is obtained from 2-naphthylamine (*Nietzki*, Ber. 19, 1281; *Zincke*, Ber. 20, 2896). 4-Amino-(1,2'-azonaphthalene),  $\text{C}_{10}\text{H}_7[2']\text{N}_2[1]\text{C}_{10}\text{H}_6[4]\text{NH}_2$ , yellowish-brown needles, m.p. 152°, is obtained from diazotised 2-naphthylamine and 1-naphthylamine hydrochloride in dilute hydrochloric acid (*Nietzki*, Ber. 20, 612).

1-Naphthylamino-azobenzene-*p*-sulphonic acid,  $\text{C}_6\text{H}_4(\text{SO}_3\text{H}) \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ , obtained by the action of sulphanic acid on diazotised 1-naphthylamine hydrochloride, gives an orange colour with alkalis and a red colour with acids (test for nitrous acid).

The *o*-azo-compounds of the 2-naphthyl-arylamines such as 1-benzeneazo-2-naphthylphenylamine,  $\text{C}_{10}\text{H}_6 \begin{array}{l} \diagup [1]\text{N}:\text{NC}_6\text{H}_5 \\ \diagdown [2]\text{NH} \cdot \text{C}_6\text{H}_5 \end{array}$ , gives ammonium bases of the pseudo-azimido-group with oxidising agents, and naphthophenazines on heating with strong mineral acids, when aniline is split off:



For the constitution of the product of the action of diazonium salts on 2-naphthylamines, of which the salts are apparently to be regarded as derivatives of 1,2-naphthaquinone, see p. 210.

6. **HYDRAZINE-COMPOUNDS OF NAPHTHALENE**. 1,1'-Hydrazo-naphthalene,  $\text{C}_{10}\text{H}_7\text{NH} \cdot \text{NHC}_{10}\text{H}_7$ , m.p. 275°, corresponds to hydrazobenzene. It is obtained by reduction of azo-naphthalene with alcoholic soda and zinc dust, and on warming with hydrochloric acid is converted into a mixture of 4,4'-diamino-1,1'-dinaphthyl, or naphthidine, and 1,1'-diamino-2,2'-dinaphthyl, or dinaphthylene (*Vesely*, Ber. 38, 136). 2,2'-Hydrazonaphthalene, m.p. 141°, isomerises in the presence of either acid or alkali to 2,2'-diamino-1,1'-dinaphthyl (see benzidine transformation, p. 145).

**Naphthyl-hydrazine**,  $\text{C}_{10}\text{H}_7\text{NHNH}_2$ , 1-compound, m.p. 117°, 2-compound, m.p. 125°, is obtained from the diazonium chlorides of the two naphthylamines by reduction with stannous chloride and hydrochloric acid (*Fischer*, Ann. 232, 236) and also from the naphthols by heating with hydrazine hydrate and hydrazine sulphite (*Hoffmann*, Ber. 31, 2909). It combines with aldehydes and ketones to give hydrazones, which give naphthindole derivatives on condensation. They

give similar derivatives to those of phenylhydrazine (pp. 151-161) (*Schlieper*, Ann. 236, 174; *Ince*, Ann. 253, 35, *etc.*). For the 2-naphthylhydrazones of the sugars, see Ber. 35, 1841. 2,3-Naphthylene-dihydrazine,  $C_{10}H_6[2,3](NHNH_2)_2$ , m.p. 156°, see *Franken*, Ber. 38, 266; J. pr. [2], 76, 205.

7. **SULPHONIC ACIDS.** When naphthalene is heated with sulphuric acid, 1- and 2-naphthalene sulphonic acids are formed. At lower temperatures (80°), the 1-acid, m.p. 90°, predominates, and at higher temperatures (160°) and excess of sulphuric acid, the 2-acid, m.p. 91°. The 1-acid is converted into the 2-acid by heating with sulphuric acid. The 2-acid forms a monohydrate, m.p. 124°, and a trihydrate, m.p. 83° (*Witt*, Ber. 48, 743). The free acids are deliquescent and crystalline. The two acids are separated from each other by means of the calcium or lead salts (*Euwe*, Rec. 28, 298). The 1-acid breaks down on heating with dilute sulphuric acid at 200° into naphthalene and sulphuric acid, but the 2-acid is unchanged by this treatment. The 1-sulphonyl chloride, m.p. 66°, b.p. 195° (13 mm.); 2-sulphonyl chloride, m.p. 78°, b.p. 201° (13 mm.) (*Fischer*, Ber. 35, 3779). When naphthalene is heated with concentrated sulphuric acid, two isomeric disulphonic acids are formed: 2,6- and 2,7-naphthalene disulphonic acids, which can be separated by crystallisation of their chlorides from benzene (*Ebert*, Ber. 9, 592). On very long heating, the 2,7-acid is converted into the 2,6-acid (*Heid*, Am. 49, 844). 1,6-Naphthalene disulphonic acid is obtained by the action of concentrated sulphuric acid at 100-110° on 2-naphthalene sulphonic acid (*Ambler*, Ind. Eng. Chem. 19, 417). 1,5-Naphthalene disulphonic acid can be obtained directly from naphthalene and sulphuric acid (*Fierz-David*, Helv. 6, 1133). Other naphthalene disulphonic acids are obtained by the sulphonation of naphthalene monosulphonic acids, by oxidation of thionaphtholsulphonic acids, from the naphthylamine disulphonic acids, *etc.* (*Armstrong*, Proc. 61, 10; 1890, 119, 126; 1893, 166; *Erdmann*, Ber. 32, 3186). By energetic sulphonation of naphthalene with fuming sulphuric acid a mixture of 1,4,6-tri- and 1,3,5,7-tetra-sulphonic acids is obtained (*Fierz-David*, Helv. 4, 381). When fused with alkali, the naphthalene sulphonic acids have their  $SO_3H$  groups converted into  $OH$ , and by heating with potassium cyanide, the corresponding cyano-naphthalenes are formed.

Chloronaphthalene sulphonic acids are obtained partly by the sulphonation of the chloronaphthalenes, and partly from the naphthylamine sulphonic acids by replacement of the  $NH_2$  group by halogen (*Armstrong*, Proc. 1890, 11; *Cleve*, Ber. 25, 2479; *Friedländer*, Chem.-Ztg. 19, 1114). Nitronaphthalene sulphonic acids are obtained by the sulphonation of the nitronaphthalenes, or by the nitration of the sulphonyl chlorides (*Erdmann*, Ann. 275, 230).

**Naphthylamine sulphonic acids** are of industrial importance, as they give useful dyes when coupled with the *bis*-diazonium salts of the benzidine series.

(a) 1-Naphthylamine, when treated, with excess of concentrated sulphuric acid at 130°, gives first 1,4-naphthylamine sulphonic acid, or naphthionic acid. This compound is also formed by the simultaneous reduction and sulphonation of nitronaphthalene by ammonium sulphite (*Piria*, Ann. 78, 31; *Friedländer*, Chem.-Ztg. 19, 1114). The acid crystallises with  $\frac{1}{2}H_2O$ , and is difficultly soluble in water; sodium salt,  $C_{10}H_6(NH_2)SO_3Na + 4H_2O$ ; when coupled with diazotised benzidine it gives *Congo red*. When Congo red is acted upon by tin and hydrochloric acid, it is decomposed to 1,2-naphthylene diamine-4-sulphonic acid. For other naphthylene-diamine sulphonic acids, see *Friedländer*, Ber. 29, 1978; Ger. Pat. 216,075).

By prolonged warming of 1-naphthylamine with sulphuric acid to 130°, instead of the 1,4-acid, the 1,5-naphthylamine sulphonic acid, or L acid, or naphthalidine acid, is obtained, and finally, the 1,6-acid, or *Cleve's acid* (*Erdmann*, Ann. 275, 192). 1,6- and 1,7-Naphthylamine sulphonic acids have been obtained by the electrolytic reduction of the corresponding nitro-sulphonic acid (*Fierz*, Helv. 3, 305). 1,8- or *peri*-Naphthylamine sulphonic acid, S acid, is obtained from the *peri*-nitro-sulphonic acid. The acid itself, and its derivatives, show a tendency

to split off water, forming *sultams*, e.g., *naphthsultam*,  $C_{10}H_7 \begin{smallmatrix} \diagup SO_2 \\ | \\ \diagdown NH \end{smallmatrix}$ , m.p. 178°, obtained from the acid by the action of phosphorus oxychloride, *Dannerth*, Am.

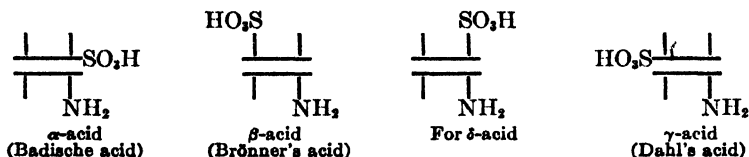
29, 1319). 1,8-Naphthsultam-2,4-disulphonic acid,  $(SO_3H)_2C_{10}H_7 \begin{smallmatrix} \diagup SO_2 \\ | \\ \diagdown NH \end{smallmatrix}$ , 1,8-

*naphthsultam-trisulphonic acid*,  $(SO_3H)_3C_{10}H_7 \begin{smallmatrix} \diagup SO_2 \\ | \\ \diagdown NH \end{smallmatrix}$  (*Dressel*, Ber. 27, 2137).

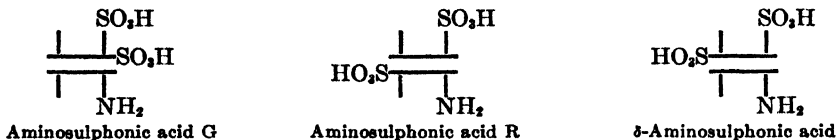
**Nitronaphthsultams**, see Ger. Pat. 210,222. For halogen derivatives of naphthsultam-quinones and other derivatives of sultams, see *Zincke*, Ann. 411, 195; 412, 78; 416, 65. On fusion with alkalis, these sultams give *peri*-aminonaphthol derivatives, and at higher temperatures, 1,8-dihydroxynaphthalenes (*Dannerth*, Am. 29, 1320).

**Dimethyl-1-naphthylamino-sulphonic acids**,  $(CH_3)_2NC_{10}H_7SO_3H$ , see *Fuss-ganger*, Ber. 35, 976. Salts of naphthionic acid condense very readily with aldehydes to give compounds of the type  $RCH:N C_{10}H_7SO_3R'$  (Ger. Pat. 124,229). 1-Naphthylamine-4,6,8-trisulphonic acid is a component of the trypanocide, *germanin* (Bayer 205).

(b) Four different 2-naphthylamine sulphonic acids are obtained by the sulphonation of 2-naphthylamine, according to the temperature (Ann. 275, 262):



They can also be obtained from the corresponding naphtholsulphonic acids by the action of ammonia. The  $\beta$ - and the F- (or  $\delta$ -) acid are particularly useful. They give beautiful reddish-blue dyes when coupled with diazotised tolidine. Some of the 2-naphthylamine disulphonic acids are also of technical importance:



For other 2-naphthylamine sulphonic acids, see *Dressel*, Ber. 27, 1193; *Fierz-David*, Helv. 6, 1133; *Frisch*, Helv. 13, 768. In those 2-naphthylamine sulphonic acids which contain a  $NH_2$  group in the *m*-position, the sulphonic acid group can readily be replaced by an amine radical by heating with an amine (Ger. Pat. 78,854).

By the action of nitrous acid on naphthionic acid, 1,4-diazonaphthalene sulphonc acid, or diazonaphthionic acid,  $C_{10}H_7 \begin{smallmatrix} [1]SO_2 \\ | \\ [4]N_2 \end{smallmatrix} O$ , is formed. By coupling with 1-naphthol, the dye roccellin (p. 624) is obtained; by coupling with 1-naphthol sulphonic acid, azorubin S is formed. By coupling various azonaphthalene-diazosulphonic acids, such as  $C_{10}H_7 \cdot N_2 \cdot C_{10}H_7 \begin{smallmatrix} N_2 \\ | \\ SO_2 \end{smallmatrix} O$ , with naphthol sulphonic acids, black azo dyes, such as *naphthol black*, are obtained.

**8. NAPHTHALENE SULPHINIC ACIDS.** These are obtained by reduction of the sulphonyl chlorides, by treating naphthalene diazonium salts with sulphur dioxide and copper powder, and by the action of sulphur dioxide on naphthalene in the presence of aluminium chloride (*cf.* p. 124 and *Gattermann*, *Ber.* **32**, 1141; *Knoevenagel*, *Ber.* **41**, 3319). 1-Naphthalene sulphinic acid,  $C_{10}H_7SO_2H$ , m.p.  $84^\circ$ ; 2-acid, m.p.  $105^\circ$  (*Otto*, *J. pr.* [2] **47**, 94). These acids react in the same way as the benzene sulphinic acids. Naphthyl-sulphones are obtained by the action of alkyl bromides on the salts of sulphinic acids (*Troger*, *J. pr.* [2], **53**, 478). When 1,8-naphthylamine-sulphinic acid is allowed to stand, it loses water and be-

comes naphthothiam,  $C_{10}H_6 \begin{array}{c} \text{SO} \\ \diagup \quad \diagdown \\ \text{NH} \end{array}$ , m.p.  $153\text{--}155^\circ$ , a compound analogous to naphthosultam. Unlike the latter, however, it is insoluble in sodium carbonate solution, but dissolves in caustic soda.

**9. NAPHTHOLS.** The hydroxy-derivatives of naphthalene behave in general like the phenols, though the hydroxyl group in the naphthols is more mobile. On heating with ammonia they are readily converted into the naphthylamines. Ester and ether formation (*Liebermann*, *Ber.* **15**, 1427; *Davis*, *Proc.* **15**, 210; *J.* **77**, 33) also occur more easily with the naphthols than with the phenols. Naphthols are found in coal-tar (*Schulze*, *Ann.* **227**, 143).

**1-Naphthol**,  $C_{10}H_7OH$ , m.p.  $94^\circ$ , b.p.  $278\text{--}280^\circ$ , is obtained by fusing 1-naphthalene sulphonic acid with caustic potash at  $300\text{--}320^\circ$ . It is also obtained from 1-naphthylamine by diazotisation, and from salts of 1-naphthylamine by heating with water to  $200^\circ$ . According to *Bucherer*, the reaction between 1- and 2-naphthol and ammonia in the presence of ammonium sulphite, which leads to 1- and 2-naphthylamine, is reversible. Thus, naphthylamines (and their derivatives) give "naphthol-sulphurous acid" with bisulphites (p. 615), which, on hydrolysis give the naphthols (or their derivatives) (*Franzen*, *Ber.* **50**, 101). A remarkable reaction is the formation of 1-naphthol by heating phenylisocrotonic acid (p. 606). 1-Naphthol is difficultly soluble in hot water, but readily soluble in alcohol and ether, and crystallises from these solvents in glistening needles. It smells like phenol and readily volatilises. Ferric chloride gives a violet precipitate of dinaphthol,  $(C_{10}H_6OH)_2$ , with the aqueous solution; alkaline iodine solution gives a violet coloration (2-naphthol gives no coloration, *Jorissen*, *Ann. chim. anal. appl.* **7**, 217). With nitrous acid, 2,1- and 4,1-nitrosonaphthol (p. 632) are formed. Chlorine in glacial acetic acid gives various chlorinated naphthols, and ketohydronaphthalenes. With sodium hypochlorite in alkaline solution, 2-chloro-1-naphthol (*Liebermann*, *Ber.* **44**, 856) is formed. With sulphuryl chloride, 4-chloro-1-naphthol is produced (*Kast*, *Ber.* **44**, 1137). Potassium chlorate and hydrochloric acid give dichloronaphthaquinone (*Darmstaedter*, *Ann.* **152**, 301). Reduction with sodium and alcohol leads to *ar*-tetrahydronaphthol (p. 642), and oxidation with alkaline permanganate gives *o*-carboxyphenylglyoxylic acid (p. 440). Acetyl-derivative,  $C_{10}H_7OCOCH_3$ , m.p.  $46^\circ$ ; carbonate, phosphate, see *Reverdin*, *Ber.* **28**, 3049.

**2-Naphthol**,  $C_{10}H_7OH$ , m.p.  $123^\circ$ , b.p.  $286^\circ$ , obtained from 2-naphthalene sulphonic acid or 2-naphthylamine, is readily soluble in hot water, and crystallises in leaflets. The solution gives a green

colouration with ferric chloride, and a precipitate of dinaphthol separates. With nitrous acid 2-naphthol gives 1,2-nitrosonaphthol (p. 632). Acetyl derivative,  $C_{10}H_7OCOCH_3$ , m.p.  $70^\circ$ . When a solution of 2-naphthol in acetic acid is mixed with mercuric acetate, a precipitate of 2-hydroxynaphthyl-mercuric acetate,  $C_{10}H_7(OH) \cdot Hg \cdot OCOCH_3$ , separates (*Bamberger*, Ber. 31, 2624).

A bismuth salt of 2-naphthol has been recommended under the name of Orpholum, as an intestinal antiseptic. The salicylic esters of 1- and 2-naphthols find a limited use as antiseptics.

*Naphthol alkyl ethers* are formed by heating the naphthol with alcohols and hydrochloric acid or sulphuric acid to  $150^\circ$ , and from the alkali salts of the naphthols by the action of alkyl halides or alkyl sulphuric acids (*Witt*, Ber. 34, 3172). In the case of the methyl ethers, the naphthols are heated with dimethyl sulphate or diazomethane. 1-Naphthol ethyl ether, b.p.  $277^\circ$ . 2-Naphthol methyl ether and -ethyl ether, m.p.  $72^\circ$  and  $37^\circ$ , are used in perfumery under the names Nerolin, New Nerolin or Jara-Jara, and Bromelia (*Jacobsen*, Ber. 26, 2706; *Bodroux*, C.r. 126, 840). 1- and 2-Dinaphthyl ether, m.p.  $110^\circ$  and  $106^\circ$  (*Graebe*, Ber. 13, 1840; *Merz*, Ber. 14, 195; *Rodonow*, J. Soc. Chem. Ind. London 42, 509). 1- and 2-Naphthyl-phenyl ethers, m.p.  $55^\circ$ , and  $93^\circ$ , are obtained by the action of phenol on the diazonaphthalenes (*Hönigschmid*, Mo. 23, 823). 1- and 2-Naphthoxy-acetic acid,  $C_{10}H_7OCH_2COOH$ , see *Spitzer*, Ber. 34, 3191.

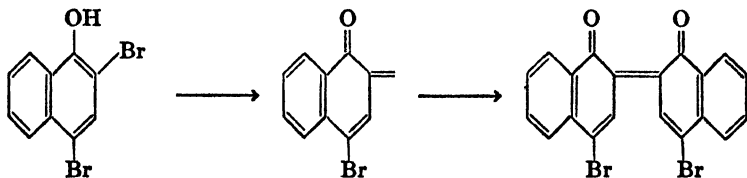
*Homologues of naphthol*, such as 2,1-methyl-naphthol,  $C_{10}H_8[2]CH_3[1]OH$ , m.p.  $61^\circ$ , and 4,1-methyl-naphthol, m.p.  $84-85^\circ$ , have been obtained from the corresponding methyl-naphthylamines through the diazonium-compounds (*Lesser*, Ann. 402, 24). 1,4-Dimethyl-3-naphthol,  $C_{10}H_8(CH_3)_2OH$ , m.p.  $136^\circ$ , is obtained from santonin (Vol. II, p. 488) (*Cannizzaro*, Gazz. 24, II, 541; Atti. R. Accad. Lincei 1895, I, 287; *Wedekind*, Ber. 31, 1675). 1,2-Methyl-naphthol,  $C_{10}H_8[1]CH_3[2]OH$ , m.p.  $110^\circ$ , is obtained from 2-dinaphthol-methane (p. 639) by reduction with zinc dust and caustic soda (cf. p. 225). Nitrous acid reacts in a curious way with 1,2-methyl-naphthol and its substitution products. *o*-Quinonitrols, or *o*-methylene-quinones (p. 340) are formed according to the conditions. 1,2-Methyl-naphthoquino-nitrol,  $C_{10}H_8[2]:O[1](NO_2)CH_3$ , m.p.  $60^\circ$ , when heated below the m.p. splits off oxides of nitrogen giving 1,2-methyl-naphthoquinol,  $C_{10}H_8[2]:O[1](OH)CH_3$ , m.p.  $89^\circ$ , a compound which can also be obtained directly from 1,2-methyl-naphthol by oxidation with chromic acid in glacial acetic acid (*Bargellini*, Atti. R. Accad. Lincei [5], 16, II, 255). The quino-nitrols are true nitro-compounds, and not esters of nitrous acid (*Fries*, Ann. 462, 1). Quinol-halides are also known, which give quinamines,  $C_{10}H_8[2]:O[1](NHR)CH_3$ , with primary amines. Thus, with aniline, 1-anilido-1-methyl-2-oxonaphthalene-dihydride (1,2), m.p.  $141^\circ$ , is formed (*Fries*, Ann. 470, 20; Ber. 54, 2925). 1,2-Naphtho-methylene-quinone,  $C_{10}H_8[2]:O[1]:CH_2$ , m.p.  $132^\circ$ , yellow needles, shows the same striking lack of reactivity as do the *o*-methylene-quinones of the benzene series (*Fries*, Ber. 39, 435; cf. also Ber. 41, 2614). It is sometimes regarded as a free radical (see Vol. IV).

*Substituted naphthols*.—Substituted 1-naphthols are obtained synthetically from the substituted phenylisocrotonic acids (cf. *Erdmann*, Ann. 275, 291). They are usually prepared by similar methods as those by which the substituted phenols are obtained (p. 197).

The bromination of 2-naphthol leads successively to the substitution of the 1, 6, and 4-positions in the naphthalene nucleus by bromine. 6-Bromo-2-naphthol is obtained from 1,6-dibromo-2-naphthol by reduction with tin and glacial acetic acid, or concentrated hydriodic acid (*Fries*, Ber. 58, 2840).

For other halogeno-naphthols and their derivatives, see *Franzen*, J. pr. [2], 103, 352; *Wheeler*, Am. 52, 4872; *Fries*, Bull. [4], 47, 1314; *Cohen*, J. 1934, 653.

By the action of silver oxide or lead dioxide, or even by careful treatment with alkalis, halogenated naphthols give dyes derived from 2,2'-dinaphthyl. They possibly have an indigoid configuration.



**Nitronaphthols.**—4,1-Nitronaphthol,  $C_{10}H_6[4](NO_2)[1]OH$ , m.p.  $164^\circ$ , and 2,1-nitronaphthol, m.p.  $195^\circ$ , are obtained by the oxidation of 4,1- and 2,1-nitrosonaphthols, respectively, with potassium ferricyanide or nitric acid (*Grandmougin*, Ber. 25, 973), or by boiling the corresponding nitronaphthylamines with caustic potash. Other nitronaphthols may be obtained from the nitronaphthylamines through the diazonium compounds (*Vesely*, Bull. [4], 33, 319). By the action of nitric acid on these nitronaphthols, or on naphthalene-1-sulphonic acid, 1-naphthylamine, or 1-naphthol-disulphonic acid, 2,4-dinitro-1-naphthol, m.p.  $138^\circ$ , is obtained (*Darmslaedter*, Ann. 152, 299). It is almost insoluble in water, and difficultly soluble in alcohol and ether. It decomposes alkali-metal carbonates and gives yellow salts with 1 equivalent of base. These dye silk a golden-yellow. The sodium salt,  $C_{10}H_5(NO_2)_2ONa + H_2O$ , is used in the dyeing industry as naphthalene yellow, or Martius' yellow. It is also used in dyeing food. The potassium salt of dinitro-naphthol-sulphonic acid,

$C_{10}H_4(NO_2)_2 \begin{matrix} [1]OK \\ [7]SO_3K \end{matrix}$ , which is obtained by the nitration of naphthol-trisulphonic acid, is naphthol yellow, or citronine A. It dyes wool and silk yellow (*Armstrong*, Proc. 1890, 16). Trinitro-1-naphthols, naphthopicric acids, see *Kehrmann*, Ber. 31, 2420; *Graebe*, Ber. 32, 2877.

1-Nitro-2-naphthol, m.p.  $103^\circ$ , is obtained by oxidation of 1-nitroso-2-naphthol (p. 632) or from nitro-2-naphthylamine by the action of caustic alkali. For other nitro-2-naphthols and -naphthol ethers, see *Friedländer*, Ber. 25, 2079; *Gaess*, J. pr. [2], 45, 614; *Kehrmann*, Ber. 31, 2418.

**Amino-naphthols** are obtained by the reduction of nitronaphthols, by the decomposition of naphthol-azo-compounds, by the action of ammonia on dihydroxy-naphthalenes, by fusing naphthylamine sulphonic acids with potash, and from naphthol-sulphonic acids, or directly from the naphthols themselves by the action of sodamide (*Sachs*, Ber. 39, 3006). In the isonuclear amino-naphthols, and particularly in 1,3-amino-naphthol, the  $NH_2$  is much more mobile than it is in the heteronuclear isomers. 1,4-Amino-naphthol,  $C_{10}H_7(NH_2) \cdot OH$ , obtained by the reduction of 1,4-nitronaphthol, or fission of 1-naphthol-orange,  $C_{10}H_7(OH) \cdot N_2 \cdot C_6H_4SO_3H$ , is very unstable, and gives 1,4-naphthaquinone on oxidation. Ethyl ether,  $C_{10}H_7(OC_2H_5)NH_2$ , m.p.  $96^\circ$ ; formyl-4-amino-1-naphthol, m.p.  $168^\circ$  (Ger. Pat. 149,022). N-Acetyl-derivative, naphthacetol, m.p.  $187^\circ$ , is particularly suitable for the preparation of true naphthol-azo dyes (p. 624); 4-acetyl-amino-1-naphthol ethyl ether, naphthacetin, m.p.  $189^\circ$  (*Henriques*, Ber. 25, 3059). 2-Amino-1-naphthol, obtained from 2,1-nitronaphthol, is oxidised in

the air to imino-oxy-naphthalene, or 1,2-naphthaquinone-imine,  $C_{10}H_6 \begin{matrix} \text{NH} \\ \text{O} \end{matrix}$  (p. 633), which separates in violet flakes. 2,1-Amino-naphthol forms anhydro bases or naphthoxazoles, with carboxylic acids (cf. p. 204, and *Michel*, Ber. 25, 3430).

1,2-Naphthaquinone-2-diazide,  $C_{10}H_6 \begin{matrix} [2] \text{N} \\ [1] \text{O} \end{matrix}$ , yellow needles, m.p.  $77^\circ$ , is obtained from chloro-2-naphthalene diazonium sulphate on standing in aq. solution, or by oxidation of the diazonium compound of 2-naphthylamine with potassium ferricyanide. 1,2-Naphthaquinone-1-diazide, m.p.  $94-95^\circ$  (*Bamberger*, J. pr. [2], 105, 251); cf. quinone-diazide, p. 245 (*Orton*, Proc. 18, 252).

1-Amino-2-naphthol, obtained by reduction of 1-nitro- or 1-nitroso-2-naphthol, or decomposition of  $\beta$ -naphthol orange, gives 1,2-naphthaquinone on oxidation. 1,3-Amino-naphthol decomposes at  $185^\circ$  (Ber. 28, 1952). 2,3-Amino-naphthol,

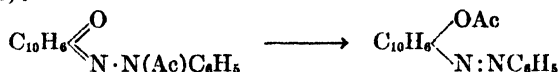


m.p. 234°, is obtained by the action of concentrated ammonia at 135–140° on 2,3-dihydroxynaphthalene (*Friedländer*, Ber. 27, 763). 1,6-Amino-naphthol, m.p. 190°, is obtained from 2-naphthol, 2,6- and 2,8-naphthol sulphonic acids. 1,5-Amino-naphthol is obtained from 1-naphthol and 1,5-naphthol sulphonic acid by fusion with sodamide. 1,8-(*peri*-)Amino-naphthol, m.p. 96°, is obtained from 1,8-naphthylamine sulphonic acid by fusion with potash (*Fichter*, Ber. 39, 3331; 42, 4748). 1,7-Amino-naphthol, m.p. 165°, see *Kehrmann*, Ber. 42, 350; *Brown*, Am. 51, 1766. For a brief description of the preparation of all 1,4-aminonaphthols, see *Middenden*, Chem. Trade J., 73, 35.

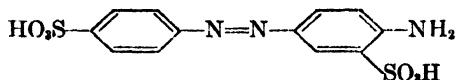
**Azonaphthols.**—The naphthols readily combine with all diazonium compounds giving azo-compounds. The 1-naphthols couple in the para-(4) or in the ortho-(2) position. However, the coupling takes place more readily in the para-position, and it is usually only when this is occupied that the coupling takes place in the ortho-position (*Witt*, Ber. 29, 2945; *Gattermann*, Ber. 30, 50; *Hantower*, Ber. 31, 2156). *o,p*-bis-Azo-compounds can also be obtained. In the case of the 2-naphthols, the diazo-group can only enter the 1-position adjacent to the OH group. In the case of 1-naphthol, 1,4-naphthol-azo-benzene, (OH)[1]C<sub>10</sub>H<sub>7</sub>[4]N:NC<sub>6</sub>H<sub>5</sub>, is first formed, and then 1-naphthol-2,4-bis-azobenzene, (OH)[1]C<sub>10</sub>H<sub>6</sub>[2,4](N:NC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>; 2-naphthol gives 2-naphthol-1-azobenzene, (OH)[2]C<sub>10</sub>H<sub>7</sub>[1]N:-NC<sub>6</sub>H<sub>5</sub>.

These substances are also obtained by the action of phenylhydrazine on the naphthaquinones (p. 631). 1,4-Naphtho-quinone-phenylhydrazine is identical with 1-naphthol-4-azobenzene. By the action of phenylhydrazine on 1,2-naphthaquinone, 1-naphthol-2-azobenzene, m.p. 128°, is obtained. This compound cannot be obtained directly from 1-naphthol. By the action of phenyl-diazonium chloride it is converted into 1-naphthol-2,4-bis-diazobenzene.

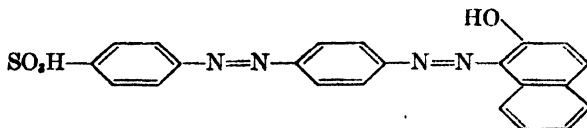
In spite of these methods of preparation, the azonaphthols, like the azophenols (p. 209), are to be regarded as true oxy-azo-compounds. The tendency for the assumption of an azo-structure is so great in the case of 1-naphthol-2-azobenzene that the acyl-phenylhydrazones first formed from 1,2-naphthaquinone and *as*-acyl-phenylhydrazines immediately isomerises to the O-acyl-compounds, which are also obtained directly by the acylation of 1-naphthol-2-azobenzene (*Auwers*, Ann. 359, 353):



The naphthol-azo-compounds are very important in the dyestuff industry. They are used almost exclusively in the form of their sulphonic acids, and are obtained (1) by the combination of the naphthols with diazotised aminosulphonic acids. Thus,  $\alpha$ -naphthol orange, OH[1]C<sub>10</sub>H<sub>7</sub>[4]·N<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H,  $\beta$ -naphthol orange, OH[2]C<sub>10</sub>H<sub>7</sub>[1]N<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H, *roccellin*, OH[2]C<sub>10</sub>H<sub>6</sub>[1]N<sub>2</sub>·C<sub>10</sub>H<sub>7</sub>SO<sub>3</sub>H, are important compounds of this class. Fast yellow G, is obtained by the sulphonation of *p*-amino-azobenzene (p. 179)

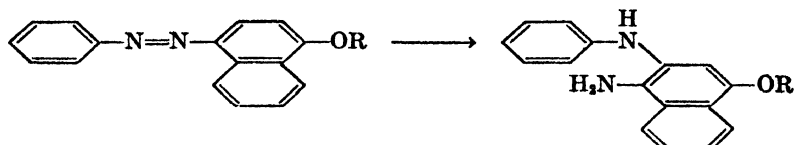


By diazotisation of fast yellow and coupling with 2-naphthol gives rise to **Biebrich scarlet**,



a scarlet dye for wool. They are also formed (2) by the combination of diazo-salts with naphthol-sulphonic acids. For dyes from naphthaetol and diazonium compounds, see *Witt*, Ber. 29, 2945. 1-Diazonaphthol-2-sulphonic acid-4 is used for the preparation of photo-tracing paper. It is bleached by light (*Schmidt*, Ber. 64, 767).

When azo-naphthols are reduced, amino-naphthols and amines are formed. Phenylazo-*p*-naphthol ether gives 2-anilino-1,4-amino-naphthol ether:



when reduced with stannous chloride. The transformation occurring here is strictly analogous to the semidine transformation of a hydroazobenzene substituted in the *p*-position.

**Naphthol sulphonic acids.**—These have been prepared in large numbers and are of technical importance. In their methods of

**1-Naphthol-monosulphonic acids**  
 $C_{10}H_7OH \cdot SO_3H$

- |   |   |                                                                            |
|---|---|----------------------------------------------------------------------------|
| 1 | 2 | <i>Schäffer's</i> $\alpha$ -acid. Ann. 152, 293.                           |
| 1 | 3 | Ber. 26, R 31.                                                             |
| 1 | 4 | <i>Neville and Winther's</i> acid. Ber. 24, 3157; 27, 3458; Ann. 273, 102. |
| 1 | 5 | L-acid. Ann. 247, 343.                                                     |
| 1 | 7 | Ber. 22, 993.                                                              |
| 1 | 8 | <i>Schöllkopf's</i> acid. Ann. 247, 306; Ber. 23, 3088.                    |

**1-Naphthol-disulphonic acids**  
 $C_{10}H_6OH \cdot SO_3H \cdot SO_3H$

- |   |   |   |                                              |
|---|---|---|----------------------------------------------|
| 1 | 2 | 4 | Disulphonic acid for Martius yellow, p. 623. |
| 1 | 2 | 7 | Ber. 25, 1400.                               |
| 1 | 3 | 7 | $\epsilon$ -Disulphonic acid. Ber. 22, 3227. |
| 1 | 4 | 6 | Ger. Pat. 41,957.                            |
| 1 | 4 | 7 | Ber. 24, 709; 29, 38.                        |
| 1 | 4 | 3 | Disulphonic acid S. Ber. 23, 3090.           |

**1-Naphthol-trisulphonic acids**  
 $C_{10}H_4 \cdot OH \cdot SO_3H \cdot SO_3H \cdot SO_3H$

- |   |   |   |   |                                                        |
|---|---|---|---|--------------------------------------------------------|
| 1 | 2 | 4 | 7 | Sulphonic acid for naphthol yellow (p. 623).           |
| 1 | 3 | 6 | 8 | Sulphonic acid for chromotrop. Ber. 24, 485; 31, 2156. |

**2-Naphthol-monosulphonic acids**  
 $OH \cdot SO_3H$

- |   |   |                                                                            |
|---|---|----------------------------------------------------------------------------|
| 2 | 1 | <i>Marschalk.</i> Bull. [4] 45, 651.                                       |
| 2 | 4 | <i>Marschalk.</i> Bull. [4] 45, 651.                                       |
| 2 | 5 | $\gamma$ -Monosulphonic acid. Ber. 22, 336.                                |
| 2 | 6 | <i>Schäffer's</i> $\beta$ -acid. Ann. 152, 296. <i>Engel</i> , Am 52, 211. |
| 2 | 7 | F- or $\delta$ -acid (p. 620). Ber. 20, 1426; 22, 724.                     |
| 2 | 8 | Croceic acid. Ber. 22, 453; 24, 654.                                       |

**2-Naphthol-disulphonic acids**  
 $OH \cdot SO_3H \cdot SO_3H$

- |   |   |   |                                            |
|---|---|---|--------------------------------------------|
| 2 | 3 | 6 | R-acid. Ber. 22, 396.                      |
| 2 | 3 | 7 | $\delta$ -Disulphonic acid. Ber. 20, 2906. |
| 2 | 4 | 8 | Disulphonic acid C. Ber. 26, 259.          |
| 2 | 6 | 8 | G-acid. Ber. 24, 707.                      |

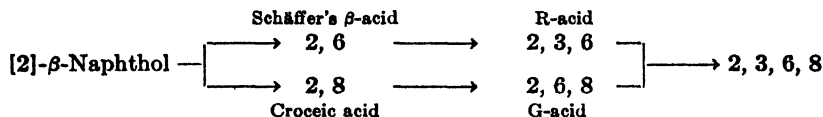
**2-Naphthol-trisulphonic acids**  
 $OH \cdot SO_3H \cdot SO_3H \cdot SO_3H$

- |   |   |   |   |                |
|---|---|---|---|----------------|
| 2 | 3 | 6 | 8 | Ber. 16, 4622. |
|---|---|---|---|----------------|

Other 2-naphthol-trisulphonic acids; see Ber. 27, 1207, 1209.

preparation and their properties they present no different features from the phenol-sulphonic acids. On the preceding page is a review of some of the more important members of this group.\*

Neville and Winther's acid, which corresponds to naphthionic acid (p. 619) and is made, in the purest state, from 1-naphthyl-carbonate and concentrated sulphuric acid, is the acid most frequently used in the manufacture of azo-dyes. R-acid and G-acid are also used. They combine with the diazo-compounds of benzene and naphthalene to give a series of ponceau and Bordeaux dyes of the most diverse shades. The most important sulphonic acids of 2-naphthol are all made by the sulphonation of the latter; the following scheme indicates the acids formed. They may be formed together, or consecutively.



Those naphthol-sulphonic acids which have a OH- and a SO<sub>3</sub>H- group in the 1,8- or *peri*-position, form anhydrides, resembling lactones, called sultones (cf.

sultams, p. 620). Naphthsultone, C<sub>10</sub>H<sub>6</sub> $\begin{array}{c} [1]O \\ | \\ [8]SO_2 \end{array}$ , m.p. 154°, b.p. above 360°,

is obtained by the decomposition of the diazo-compound of *peri*-naphthylamino-sulphonic acid. The sultone dissolves in hot alkalis, forming salts of *peri*-naphtholsulphonic acid. Sultones are also obtained from 1-naphthol-3,8- and -4,8-di- and 3,6,8-trisulphonic acids. For sulphonyl chlorides of 1- and 2-naphthol, see Pollak, Mo. 49, 187, 203.

*Aminonaphthol-sulphonic acids* are formed by reductive fission of the azo-compounds of naphtholsulphonic acids, from naphthylamine-polysulphonic acids by partial fusion with alkali; from diamidonaphthalene-sulphonic acids by heating with sodium sulphite, and then with caustic soda. They are also obtained by reduction and sulphonation of nitroso-naphthols. These two processes can be carried out together by treatment of the nitrosonaphthols with sulphurous acid (Böniger, Ber. 27, 23, 3050). 1,2-Nitroso-naphthol gives 1,2,4-aminonaphthol sulphonic acid, C<sub>10</sub>H<sub>6</sub>[1]NH<sub>2</sub>[2]OH[4]SO<sub>3</sub>H, in this way. The isomeric 2,1,4-acid, C<sub>10</sub>H<sub>6</sub>[1]OH[2]NH<sub>2</sub>[4]SO<sub>3</sub>H, is obtained by oxidation, even by atmospheric

oxygen, of imino-oxo-naphthalene sulphonic acid, SO<sub>3</sub>HC<sub>10</sub>H<sub>5</sub> $\begin{array}{c} O \\ \diagup \\ NH \end{array}$ , a blackish-

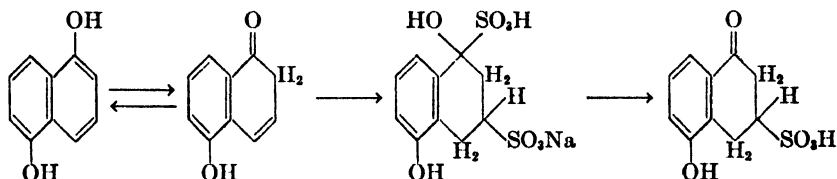
violet dye, fast to light and washing (Reverdin, Ber. 25, 1400; 26, 1279). The 2,1,6-acid is used in photography as a developer under the name Eikonogen. 2-Amino-8-naphthol 6-sulphonic acid G (Ger. Pat. 62,934; Tauber, Ber. 29, 2267), 1-amino-8-naphthol-3,6-disulphonic acid H (Ger. Pat. 67,062 and 69,722), 2-amino-5-naphthol-7-sulphonic acid, or J acid (Ger. Pat. 188,505) are important in the dyeing industry because they impart to the azo-dyes of which they form part, the power to dye vegetable fibres directly, Baltegay, Bull. [4], 33, 1481. Some of the 1,8-aminonaphthol-sulphonic acids are used as in the production of black dyes for wool. For 2-amino-5-naphthol-1-sulphonic acid, see Ger. Pat. 233,105. For other aminonaphthol-sulphonic acids, see Bucherer, J. pr. [2], 80, 201; Ruggli, Helv. 13, 748, 756.

*Dihydroxynaphthalenes*.—The ten possible isomers are all known. The most important are the naphthohydroquinones, obtained by the reduction of the naphthaquinones. 1,2-Naphthohydroquinone, C<sub>10</sub>H<sub>6</sub>[1,2](OH)<sub>2</sub>, m.p. about 60°, is obtained from 1,2-naphthaquinone by boiling with sulphurous acid. It is a strong caustic, and dissolves in alkalis with a yellow colour, which turns bright green on exposure to air. 1,4-Naphthohydroquinone, C<sub>10</sub>H<sub>6</sub>[1,4](OH)<sub>2</sub>, m.p. 176°, is obtained by reduction of 1,4-naphthaquinone with hydriodic acid and phosphorus, or zinc and hydrochloric acid. It is readily oxidised back to 1,4-

\* See R. Nietski, *Chemie der organischen Farbstoffe*, 4th ed., Springer, Berlin, 1901; F. Mayer, *Chemie der organischen Farbstoffe*, 3rd ed., Springer, Berlin, 1934.

naphthaquinone by chromic acid. **2,6-Dihydroxynaphthalene**, m.p. 218°, is obtained by fusing Schäffer's 2-naphthol-sulphonic acid with potash. On oxidation with lead dioxide in benzene solution it gives 2,6- or *amphi*-naphthaquinone (p. 631), from which it can be reobtained by reduction with dilute hydriodic acid (Willstätter, Ber. 40, 1410). **2,3-Dihydroxynaphthalene**, m.p. 159°, monomethyl ether, m.p. 108°, has a similar physiological action to guaiacol (p. 219) (Friedländer, Ber. 27, 762; Mo. 23, 513; Ger. Pat. 133,459). See also Erdmann, Ann. 247, 356; Clausius, Ber. 23, 519, etc. **1,3-Dihydroxynaphthalene**, or naphthoresorcinol, m.p. 124°, is obtained from 1,3,4-aminonaphthol-sulphonic acid. When fused with alkali it gives *o*-toluic acid (see p. 292 and Friedländer, Ber. 29, 1611). **2-Phenyl-1,3-dihydroxynaphthalene**, m.p. 166°, is obtained by the action of concentrated sulphuric acid on  $\alpha,\gamma$ -diphenylacetoacetic ester. It readily takes up oxygen, giving phenylhydroxy-1,4-naphthaquinone. **1,5-Dihydroxynaphthalene**, m.p. 258–260°; **1,6-dihydroxynaphthalene**, m.p. 135.5° (Fischer, J. pr. [2], 94, 1; Fuchs, Ber. 55, 658). **1,7-Dihydroxynaphthalene**, m.p. 175°, see Friedländer, Ber. 29, 40; **2,7-Dihydroxynaphthalene**, m.p. 190°, see Nietzki, Ber. 30, 1119; Fischer, J. pr. [2], 94, 1. **1,8-(peri)Dihydroxynaphthalene**, m.p. 140°, from naphthsultone (see above) by fusion with potash (Erdmann, Ann. 247, 356). **1,8-Dihydroxynaphthalene-3,6-disulphonic acid** is called chromotropic acid. It is obtained by fusing the corresponding naphthol-trisulphonic acid with potash, and is important as a component of the valuable *o*-hydroxyazo-dyes (Hantower, Ber. 31, 2156), or chrome-dyes. After dyeing they become extraordinarily fast to light and washing when treated with chromium salts. For the constitution of the chromium lake, see Rosenhauer, Ber. 62, 2717.

**1,5- and 2,7-Dihydroxynaphthalenes** combine with sodium bisulphite as if they existed in the tautomeric form of the dihydrogenated ketone. Thus, 1,5-dihydroxynaphthalene is in equilibrium with 1-oxo-5-hydroxy-1,2-dihydronaphthalene, which, on prolonged boiling with sodium bisulphite adds on one molecule of this salt to the keto-group, and a second molecule across the double bond between C<sub>3</sub> and C<sub>4</sub>. The bisulphite compound of 1-oxo-5-hydroxy-1,2,3,4-tetrahydronaphthalene-3-sulphonic acid thus obtained, readily splits off a molecule of sodium bisulphite with formation of the tetralone compound (Fricks, Ber. 55, 568):



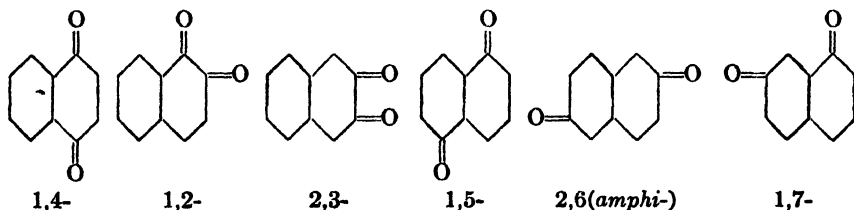
$\alpha$ - and  $\beta$ -Hydrojuglone are *trihydroxynaphthalenes*. They occur in the green shells of unripe walnuts, *Juglans regia* (Mylius, Ber. 18, 463, 2567).  **$\alpha$ -Hydrojuglone**, C<sub>10</sub>H<sub>6</sub>[1,4,5](OH)<sub>3</sub>, m.p. 169°, is also obtained by the reduction of juglone (p. 630), to which it is rapidly oxidised when its solution is exposed to the air. On distillation it is converted into  **$\beta$ -hydrojuglone**, m.p. 97°, which is not oxidised to juglone, but is converted back into the  $\alpha$ -compound by alcoholic hydrogen chloride. **1,2,4-Trihydroxynaphthalene**, m.p. 154°, is obtained in the form of its triacetate, m.p. 134°, by the action of acetic anhydride and sulphuric acid on 1,4- or 1,2-naphthaquinone (Thiele, Ann. 311, 345). **1,3,6-Trihydroxynaphthalene**, m.p. 95° (Meyer, Ber. 38, 3945).

**1,4,5,8-Tetrahydroxynaphthalene**, m.p. 190°, is obtained by reduction of naphthazarine (p. 630) with zinc dust or sodium hydrosulphite. With stannous chloride, on the other hand, **1,4-dioxo-5,8-dihydroxy-1,2,3,4-tetrahydronaphthalene**, m.p. 153°, is formed, which can also be obtained synthetically from succinic anhydride, hydroquinone, and aluminium chloride (Zahn, Ann. 462, 72). **1,4,5,6-Tetrahydroxynaphthalene**, m.p. 180°, is obtained by reduction of *o*-naphthazarine. When *iso*-naphthazarine is reduced, **1,2,3,4-tetrahydroxynaphthalene** is obtained, which is very readily reconverted into *isonaphthazarine*. On further reduction, *iso*-naphthazarine gives **1,2,3-trihydroxynaphthalene**, or naphthopyrogallol (Zincke, Ann. 307, 16).

**Thionaphthols** are obtained by the reduction of naphthalene sulphonyl chlorides or from the diazonaphthalenes. **Thionaphthol**, or naphthyl-mercaptan,  $C_{10}H_7 \cdot SH$ , 1-liquid, b.p.  $286^\circ$ , 2-m.p.  $81^\circ$ , b.p.  $286^\circ$  (*Krafft*, Ber. 26, 2816; *Leuckart*, J. pr. [2], 41, 179; *Bourgeois*, Rec. 18, 426). The lead salt,  $(C_{10}H_7[2]S)_2Pb$ , when heated with bromobenzene gives **phenyl-2-naphthyl sulphide**, m.p.  $51^\circ$ . When heated by itself the lead salt gives various **dinaphthyl sulphides**, which can also be obtained by other methods (*Krafft*, Ber. 26, 2816). **2-Naphthyl sulphur chloride** is obtained by the action of the calculated quantity of chlorine on 2-naphthyl-mercaptan. It is a crystalline powder melting between  $50^\circ$  and  $60^\circ$ , which is easily converted into the disulphide. With an excess of chlorine 1-chloro-2-naphthyl sulphur chloride is obtained, which is stable (*Zincke*, Ber. 51, 751). **1,4-Naphthol-mercaptan**, needles, m.p.  $114^\circ$ , is readily obtained by reduction of 1,4-naphthol sulphonyl chloride. It readily passes into the disulphide, m.p.  $152^\circ$  (*Zincke*, Ber. 48, 120). By the action of sulphur chloride on 2-naphthol, **dihydroxydinaphthyl sulphide**,  $S(C_{10}H_6 \cdot OH)_2$ , m.p.  $216^\circ$  is obtained.

It is readily oxidised to a dehydro-compound,  $S \begin{matrix} \nearrow C_{10}H_6O \\ \searrow C_{10}H_6O \end{matrix}$ , m.p.  $155^\circ$  (*Henriques*, Ber. 27, 2993; *Marckwald*, Ber. 28, 114). When this is treated with zinc and glacial acetic acid, *iso*-2-naphthol sulphide, m.p.  $159^\circ$ , is formed. For the isomerism of the two naphthol sulphides, see *Lesser*, Ber. 56, 963; *Hinsberg*, Ber. 56, 1735; *Lesser*, Ber. 56, 1802. **Naphthalene dihydrogen sulphide**,  $C_{10}H_8(SH)_2$ , see *Braun*, Ber. 25, 2735. **1,4-Aminonaphthyl-mercaptan**, m.p.  $91-93^\circ$ , see *Zincke*, Ber. 45, 471.

**10. QUINONES.** Theoretically six different naphthaquinones can exist, three mononuclear quinones, corresponding to the benzoquinones, and three binuclear:



There are also diquinones in which both nuclei of the naphthalene have two quinone carbonyl groups.

Of the naphthaquinones containing two carbonyl groups only the 1,4- or  $\alpha$ -, the 1,2- or  $\beta$ -, and the 2,6- or *amphi*-naphthaquinones, and a derivative of 2,3-naphthaquinone have been prepared up to the present.

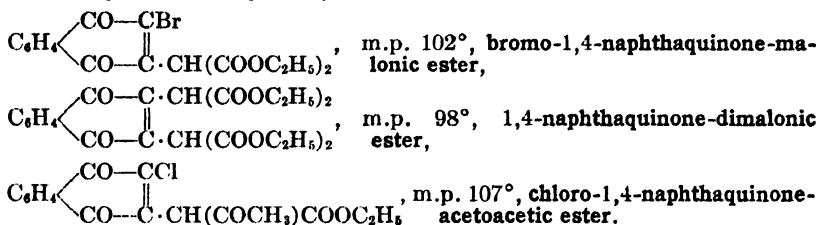
**1,4-( $\alpha$ )-Naphthaquinone**,  $O:[1]C_{10}H_6[4]:O$ , m.p.  $125^\circ$ , crystallises from alcohol in yellow, rhombic tablets, which sublime even below  $100^\circ$ . It has the characteristic quinone smell, and is readily volatile in steam. It is obtained: (1) by oxidation of naphthalene with chromic acid in glacial acetic acid solution, or by electrolytic oxidation (*de Bottens*, Z. Elektrochem. 8, 673); (2) more readily by oxidation of 1,4-diamino- or 1,4-dihydroxy-naphthalene, 1,4-aminonaphthol (*Zincke*, Ann. 286, 70), 1-naphthylamine, etc., with sodium dichromate and sulphuric acid (*Schniter*, Ber. 20, 2283). (3) Benzene-azone-naphthol is decomposed by lead dioxide and sulphuric acid in the cold into phenyl-diazonium sulphate and 1,4-naphthaquinone (*Lauth*, C.r. 112, 1512).

1,4-Naphthaquinone is oxidised to phthalic acid by nitric acid, and

when reduced it gives 1,4-naphthohydroquinone. With nitrogen trioxide in the cold it gives 1,3-diketohydrindene nitrosite (see p. 599). Its compounds with phenylhydrazine and hydroxylamine are dealt with under nitrogen-containing derivatives of naphthaquinone (p. 631).

**Substituted 1,4-naphthaquinones.**—1,4-Naphthaquinone adds on two atoms of chlorine or bromine, but the addition products soon lose HCl and HBr and give 2-chloro- and 2-bromo-1,4-naphthaquinone, m.p. 117° and 130°. 2,3-Dichloro- and 2,3-dibromonaphthaquinone, m.p. 193° and 218°.

As in the case of the 1,2-dihalogeno-indones (p. 596), the halogen atoms in these halogeno-quinones can be readily exchanged for other groups. For example, from the dihalogeno-1,4-naphthaquinones and sodio-acetoacetic ester or sodio-malonic ester, beautiful red- and blue-coloured compounds are obtained, which then pass into compounds, such as



By further transformations these compounds give rise to many derivatives of the naphthaquinone series (Graebe, Ber. 33, 566; Michel, Ber. 33, 2402; Liebermann, Ber. 34, 1543). By condensation of 2,3-dichloro-1,4-naphthaquinone with resorcinol or orcinol and sodium ethylate, derivatives of phenylene-naphthylene-

oxide,  $\text{C}_6\text{H}_4 \begin{cases} \text{CO}-\text{C} \\ \text{CO}-\text{C}=\text{O} \end{cases} \text{C}_6\text{H}_4\text{OH}$ , are obtained. This compound is closely connected with the *brasanes*, which are decomposition products of brasilin (Liebermann, Ber. 32, 924; Kostanecki, Ber. 41, 2373).

Hypochlorous acid converts 1,4-naphthaquinone into diketo-tetrahydro-naphthylene oxide,  $\text{C}_6\text{H}_4 \begin{cases} \text{CO}-\text{CH} \\ \text{CO}-\text{CH} \end{cases} \text{O}$ , which readily takes up the elements of water,

HCl, and aniline by breaking of the ethylene oxide bond. The initial products are very varied and give rise to: **hydroxynaphthaquinone**, chloro-hydroxy-naphthaquinone, anilido-hydroxynaphthaquinone, hydroxynaphthaquinone anil, and other substances; see Zincke, Ber. 25, 3599.

**Naphthafuchsone**, m.p. 179°,  $\text{O}:[1]\text{C}_{10}\text{H}_6[4]:\text{C}(\text{C}_6\text{H}_5)_2$ , may be regarded as a derivative of 1,4-naphthaquinone. It is obtained by the condensation of 1-hydroxy-2-naphthoic acid and benzilic acid, removing carbon dioxide and heating the hydroxy-carbinol-acid obtained with alkali (Zaleska-Masurkiewicz, Ber. 45, 1429).

**Amino-derivatives.**—When 1,4-naphthaquinone is heated with primary amines, alkyl- or aryl-aminonaphthaquinones are formed: **2-anilino-1,4-naphthaquinone**,  $\text{C}_{10}\text{H}_7\text{O}_2[2]\text{NHC}_6\text{H}_5$ , red needles, m.p. 191°. **2-Amino-1,4-naphthaquinone**, m.p. 203°, is obtained, together with the isomeric hydroxy-1,4-naphthaquinone-imine (p. 633), by boiling amino-1,4-naphthaquinone-imine with water (Kehrmann, Ber. 27, 3337; cf. Ber. 28, 348).

**Hydroxy-naphthaquinones.**—**2-Hydroxy-1,4-naphthaquinone**, *naphthalinic acid*, m.p. 192–195°,  $\text{C}_{10}\text{H}_7\text{O}_2[2]\text{OH}$ , is obtained by the oxidation of 1,4-naphthaquinone with alkaline hydrogen peroxide (Teichner, Ber. 38, 3376) and by boiling anilido-naphthaquinone with dilute caustic soda, or by boiling hydroxy-naphthaquinone-anil with alcohol and sulphuric acid. In addition to the *p*-quinoid configuration of naphthalinic acid, an *o*-quinoid structure is possible. In the solid state only one form is known, while in solution some of the *o*-quinoid form is produced (Fieser, Am. 48, 2922, 3201; 50, 439). **2-Hydroxy-1,4-naphthaqui-**

none is found in nature as a colouring matter in henna leaves. It is called *lawsone* (Vol. II, p. 426). 2-Phenyl-3-hydroxy-1,4-naphthaquinone, m.p. 147°, is obtained from 2-phenyl-1,3-dihydroxynaphthalene by oxidation with atmospheric oxygen in alkaline solution (*Volhard*, Ann. 296, 18). Iodoxy-1,4-naphthaquinone, *iodonaphthalinic acid*,  $C_{10}H_6O_5[2]OH[3]I$ , is obtained by iodination of naphthalinic acid (*Kehrmann*, Ber. 28, 348). The *o*-hydroxy- and *o*-amino-naphthaquinone derivatives give dyes of the paradiazine and paroxazine series with *o*-diamines and *o*-hydroxyamines (cf. also the corresponding naphthaquinone-anils) (*Kehrmann*, Ber. 28, 353).

5-Hydroxy-1,4-naphthaquinone, *juglone*, m.p. 150° (decomp.), yellowish to reddish-brown prisms, is found in nature in walnut shells (*Tommasi*, Gazz. 50, I, 263) and other green parts of the walnut tree. It is accompanied by hydrojuglone (1,4,5-trihydroxy-naphthalene). It is obtained artificially by the oxidation of  $\alpha$ -hydrojuglone with ferric chloride, and by the oxidation of 1,5-dihydroxy-naphthalene with chromic acid (*Bernthsen*, Ber. 20, 934). It is also obtained by the oxidation of the product of reduction of 1,8-amino-hydroxynaphthalene-4-azobenzene sulphonic acid (*Friedländer*, Mo. 23, 513). It dissolves in alkalis with a violet colour. When oxidised with nitric acid it gives dinitro-hydroxy-phthalic acid, *juglonic acid* (*Bernthsen*, Ber. 19, 164). For halogen derivatives of juglone, see *Wheeler*, Am. 41, 833). Plumbagin is apparently a 5-hydroxy-2-methyl-1,4-naphthaquinone (*de Buruaga*, An. soc. espan. fisica quim. 31, 185). *Lapachol* is a derivative of 3-hydroxy-1,4-naphthaquinone. It is the colouring matter of lapacho and taiga woods; *lomatiol*, which occurs in the seeds of species of *Lomatia* is also a derivative of this compound. The former is 2-( $\gamma,\gamma$ -dimethyl-allyl)-3-hydroxy-1,4-naphthaquinone, m.p. 140° (*Monti*, Gazz. 45, II, 51; *Fieser*, Am. 49, 857); the latter is 2-[ $\gamma,\gamma$ -dimethyl- $\gamma$ -hydroxy-propene(1,2)]-3-hydroxy-1,4-naphthaquinone. Both substances are yellow.

Dihydroxy-1,4-naphthaquinone, *hydroxyjuglone*, m.p. 220° (decomp.), is obtained by atmospheric oxidation of an alkaline solution of juglone. An isomeric 5,8-dihydroxy-1,4-naphthaquinone, naphthalizarin, naphthazarine, or alizarin black, is formed from 1,5- and 1,8-dinitronaphthalene by heating with conc. sulphuric acid and reducing agents (p. 614 and *Schunck*, Ber. 27, 3462; Ger. Pat. 76,922; *Fritzsch*, Ann. 286, 26). Its constitution is arrived at from the fact that it forms a diboric ester and complex salts with tin (*Dimroth*, Ann. 446, 123; *Pfeiffer*, Ber. 60, 111). It is obtained synthetically from hydroquinone, maleic anhydride, and aluminium chloride (*Zahn*, Ann. 462, 81). It is a useful substantive dye. For the bromination of naphthazarine, see *Wheeler*, Am. 49, 2825. When oxidised with manganese dioxide and sulphuric acid, naphthazarine gives naphthopurpurin, 5,7,8-trihydroxy-1,4-naphthaquinone (*Jaubert*, C. r. 129, 684; *Zahn*, Ann. 462, 72). 5,6-Dihydroxy-1,4-naphthaquinone, m.p. 201–202°, (*o*-naphthazarine) is the naphthalene homologue of alizarin. It is obtained from 6-hydroxy-1,4-naphthaquinone through the 5-nitro compound, reduction to the amino-compound, and oxidation with ferric chloride. Its dyeing properties are not so good as those of naphthazarine (*Dimroth*, Ann. 456, 177). A 2,3-dihydroxy-1,4-naphthaquinone obtained from 1,2-naphthaquinone by the action of small quantities of bleaching powder, is called isonaphthazarine. It can also be obtained by heating 2,3-hydroxyanilino-1,4-naphthaquinone with bromine (*Zincke*, Ber. 25, 409, 3606). On reduction *iso*-naphthazarine gives tetra- and tri-hydroxynaphthalene (p. 627), and on oxidation tetraketonaphthalene,  $C_{16}H_8(CO)_4$ , which is partially reconverted into *iso*-naphthazarine when heated. Phenyl-glyoxyl-*o*-carboxylic acid is also formed in the oxidation of *iso*-naphthazarine. With hydroxylamine it gives a dioxide, m.p. 228°, which gives dinitroso-1,4-naphthaquinone,  $C_{10}H_4[C_2O_2(NO)_2]$ , on oxidation (*Zincke*, Ann. 307, 1). Isonaphthazarine is closely related to carminazarine, obtained by oxidation of carminic acid (*Dimroth*, Ann. 399, 1; Ber. 42, 1612). It is 2,3,7-trihydroxy-5-methyl-8-carboxy-1,4-naphthaquinone. For 6,7-dihydroxy-1,4-naphthaquinone, see *Friedländer*, Mo. 23, 513.

2,6- and 2,7-Dihydroxy-1,4-naphthaquinone can be obtained by the action of acetic anhydride and sulphuric acid on 6- and 7-hydroxy-1,2-naphthaquinones, the tetracetyl derivatives being first formed (*Dimroth*, Ann. 399, 36).

1,4-Binaphthaquinone,  $C_{10}H_6[1,4]O_2 \cdot C_{10}H_6[1,4]O_2$ , m.p. 260–265°, is obtained by oxidation of 4-acetamino-1-naphthol (*Witt*, Ber. 30, 2663; *Ullmann*, Helv. 9, 442).

**1,4,5,8-Naphthadiquinone**, m.p. 220°, which is almost colourless, has a quinoid structure in both nuclei of naphthalene, and is obtained by dehydrogenation of naphthazarine with lead tetraacetate (*Zahn*, Ann. 462, 72).

**1,2-Naphthaquinone**,  $C_{10}H_6[1,2]O_2$ , is obtained by the oxidation of 2-amino-1-naphthol (p. 623) with ferric chloride (*Groves*, J. 45, 291; *Witt*, Ber. 21, 3472). It forms red needles which decompose at 115–120°. In contrast to the *p*-quinones it has no smell and is not volatile. It resembles anthraquinone and more still phenanthraquinone. Like the latter, it shows the reactions of an *o*-diketone. The oxidising power of 1,2-naphthaquinone is less than that of benzoquinone.

Like 1,4-naphthaquinone it forms addition products with two atoms of chlorine and bromine. These split off the halogen acid, forming chloro- and bromo-1,2-naphthaquinone. **3,4-Dichloro- and -dibromo-1,2-naphthaquinone**, m.p. 91° and 173°, respectively. **1,2-Naphthaquinone-malonic ester**,  $C_6H_4[C_4O_2H \cdot CH \cdot (COOR)_2]$ , m.p. 108°. **3-Chloro-1,2-naphthaquinone-acetoacetic ester**, m.p. 175°, see *Liebermann*, Ber. 32, 264; *Hirsch*, Ber. 33, 2412.

By the action of small quantities of bleaching powder on 1,2-naphthaquinone, *iso*-naphthazarine, and 2,3-dihydroxy-1,4-naphthaquinone are formed, together with various other products. The transformation of hydroxy- or amino-1,2-naphthaquinone derivatives into hydroxy-1,4-naphthaquinone derivatives is a common phenomenon (*cf.* hydroxy-1,4-naphthaquinone-anil, p. 633). With excess of bleaching powder, 1,2-naphthaquinone undergoes ring fission, and phenyl-glyceric-*o*-lactone is formed (pp. 440, 610). In a similar way 3-nitro-1,2-naphthaquinone, obtained by nitration of 1,2-naphthaquinone, is converted into an *o*-derivative of benzene when treated with chlorine and water. On the other hand, 3,4-dichloro-1,2-naphthaquinone (see above) first undergoes transformation into dichloro-hydroxy-indene-carboxylic acid (p. 610) when treated with alkali. 1,2-Naphthaquinone is oxidised by ferric chloride to an oxide,  $O(C_{10}H_6O_2)_2$ , m.p. 245° (*Wickelhaus*, Ber. 30, 2199), and by permanganate to phthalic acid. Sulphurous acid reduces it to 1,2-naphthohydroquinone (p. 626) and hydrogen iodide to 2-naphthol (*Japp*, J. 63, 774).

**6-Bromo-4-chloro-1-methyl-2,3-naphthaquinone**,  $C_{10}H_5[6]Br[4]Cl[1]CH_3[2,3]O_2$ , yellow prisms, decomp. 220°, is obtained by the action of iodine on the lead salt of the corresponding 2,3-dihydroxy-naphthalene. It is odourless and non-volatile. It is reduced by zinc dust and glacial acetic acid partly to the corresponding dihydroxy-naphthalene. It combines with *o*-phenylene-diamine, like the *o*-diketones, to give a derivative of naphthophenazine (*Fries*, Ber. 42, 3375).

**2,6- or *amphi*-Naphthaquinone**,  $C_{10}H_6[2,6]O_2$ , forms reddish-yellow crystals, decomp. 130–135°, and is produced by the oxidation of 2,6-dihydroxy-naphthalene in benzene solution with lead dioxide. It is non-volatile and odourless, and differs from the usual naphthaquinones by being a stronger oxidation agent. It is reduced by dilute hydriodic acid to 2,6-dihydroxy-naphthalene, with which it combines to give a bluish-green quinhydrone, decomp. 124°. Its dichloro-substitution product, **1,5-dichloro-*amphi*-naphthaquinone**, m.p. 206°, is more stable than the *amphi*-naphthaquinone itself, the latter being readily affected by dilute acids and alkalis. The dichloro-compound is obtained in a similar way to 1,5-dichloro-2,6-dihydroxy-naphthalene (*Willstätter*, Ber. 40, 1406, 3971).

For hydrogenated naphthaquinones and their stereoisomeric forms, see *Alder*, Ann. 501, 247.

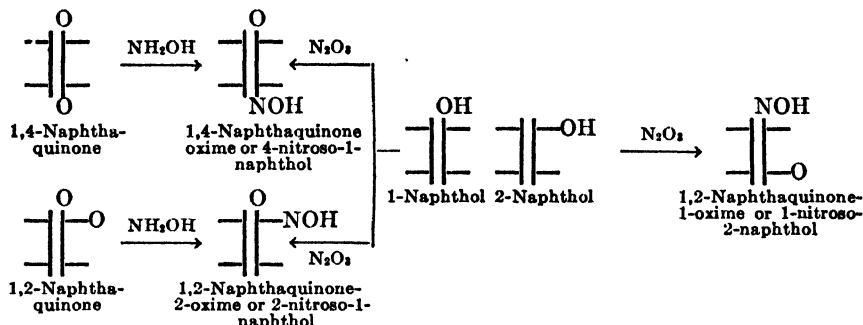
### Nitrogenous Derivatives of Naphthaquinones

**1. NAPHTHAQUINONE-PHENYLHYDRAZONES:** Unlike the benzquinones, both 1,4- and 1,2-naphthaquinone forms phenylhydrazones with phenylhydrazine (*McPherson*, Ber. 28, 2414). The quinone-phenylhydrazones are identical with the benzene-azonaphthols (p. 624) (*Farmer*, Ber. 32, 3100). The reaction products of *as*-acylphenylhydrazines on 1,2-naphthaquinone are to be regarded as *O*-acylated azonaphthols (p. 624 and *Auwers*, Ber. 40, 2156; Ann. 359, 353). On the other hand 1,4-naphthaquinone gives other products with *as*-



benzoyl- or -methyl-phenylhydrazine, viz.,  $C_{10}H_7 \cdot \text{C}(=\text{O})\text{NN}(\text{COC}_6\text{H}_5)\text{C}_6\text{H}_5$ , and  $C_{10}H_7 \cdot \text{C}(=\text{O})\text{NN}(\text{CH}_3)\text{C}_6\text{H}_5$ , while  $C_{10}H_7 \cdot \text{C}(=\text{O})\text{N}=\text{NC}_6\text{H}_5$  and  $C_{10}H_7 \cdot \text{C}(=\text{O})\text{N}:\text{NC}_6\text{H}_5$  are obtained by benzoylation and methylation of 1,4-naphthol-azo-benzene (*McPherson*, Am. 22, 364).

**2. NAPHTHAQUINONE-OXIMES, NITROSONAPHTHOLS.** When boiled with hydroxylamine hydrochloride in alcoholic solution, 1,4- and 1,2-naphthaquinones form naphthaquinone-oximes, which can also be obtained from the two naphthols by the action of nitrous acid, and are therefore to be regarded also as nitrosonaphthols:  $C_{10}H_7(\text{O})(\text{NOH})$  or  $C_{10}H_7(\text{OH})(\text{NO})$  (*cf.* nitrosophenols, p. 202). There are thus three isomeric compounds, of which the genetic connection is shown in the following diagram:



By isomerisation of nitronaphthalenes, nitrosonaphthols are also formed. Thus, when 2-nitronaphthalene is warmed with alcoholic potash, 2-nitroso-1-naphthol is formed. 1-Nitronaphthalene gives similarly 1-nitroso-4-naphthol (*Meisenheimer*, Ann. 355, 299). When 1,5-, 1,6-, and 1,8-dinitronaphthalene are treated with fuming sulphuric acid, 5-, 6-, and 8-nitro-1-nitroso-4-naphthol (p. 614 and *Graebe*, Ann. 335, 139, 145) are formed. 1,3,8-Nitronaphthalene disulphonic acid isomerises to nitrosonaphthol disulphonic acid with alkali (*Meisenheimer* Ber. 36, 4164; *Graebe*, Ber. 32, 2876). All three isomeric nitrosonaphthols are weak acids. On oxidation they give the corresponding nitronaphthols.

4-Nitroso-1-naphthol, 1,4-naphthaquinone-oxime, colourless needles, m.p.  $190^\circ$ , and 2-nitroso-1-naphthol, 1,2-naphthaquinone-2-oxime, yellow needles, m.p.  $162^\circ$ – $164^\circ$  (decomp.) (*Meisenheimer*, Ber. 36, 4165). 1,2-Naphthaquinone-oxime is best prepared from 1-hydroxy-2-naphthoic acid (p. 636) by the action of nitrous acid, a carboxyl group being split off (*Reverdin*, Ber. 26, 1280). 1-Nitroso-2-naphthol, 1,2-naphthaquinone-1-oxime, yellowish-brown prisms, m.p.  $106^\circ$ , precipitates a number of metals from their salts, and can be used for the separation of nickel from cobalt, iron from aluminium, and for the estimation of copper (*Ilinski*, Ber. 18, 2728; *von Knorre*, Ber. 20, 283). It can also be used as a reagent for phenols which have two free ortho positions, but a para-position occupied, with respect to the OH group. When a solution of phenol is treated with alkaline 1-nitroso-2-naphthol, and an oxidising agent, a carmine red colour is produced, which can be extracted by amyl alcohol (*Gerngross'* reaction, Ber. 66, 435; *cf.* Biochem. Z. 259, 240). The oxime of 1,2-naphthaquinone forms complex salts with iron salts, which have a deep green colour; it can be used as a mordant dye on a fabric treated with an iron mordant. Thus the iron salt of 1-nitroso-2-naphthol-6-sulphonic acid,  $C_{10}H_5[6](\text{SO}_3\text{H})[2]\text{O}[1](\text{NOH})$ , obtained by the action of nitrogen trioxide on Schäffer's 2-naphthol sulphonic acid, is the wool dye, naphthol green (*Hoffmann*, Ber. 24, 3741). For the product of the action of nitrogen dioxide on Schäffer's  $\beta$ -acid, see *Nietzki*, Ber. 30, 187.

The ethers of the nitroso-naphthols, which can be obtained from the silver salts by the action of alkyl iodides, and also, partially, from the quinones by the action

of alkyl-hydroxylamines (*Goldschmidt*, Ber. 18, 571, 2225), give amino-naphthols on reduction, which agrees with the "oxime formula" for the nitrosonaphthols.

1,4-Naphthaquinone-dioxime,  $C_{10}H_8(NO)_2$ , m.p. 207°, is obtained by the action of hydroxylamine hydrochloride on 1-nitroso-4-naphthol (*Nietzki*, Ber. 21, 433).

1,2-Naphthaquinone-dioxime,  $C_{10}H_8(NO)_2$ , m.p. 149°, is obtained by the action of hydroxylamine hydrochloride on 2,1- or 1,2-nitrosonaphthol (*Goldschmidt*, Ber. 17, 2064; *Ilinski*, Ber. 17, 2582). When warmed with alkalis it

forms an anhydride,  $C_{10}H_8 \begin{matrix} [1]N \\ \diagup \quad \diagdown \\ [2]N \end{matrix} O$ , m.p. 78°, which can be regarded as naphtho-furazane. Naphthylene-diamines are obtained by reduction of naphthaquinone-dioximes.

3. NAPHTHAQUINONE-CHLORIMINES (*cf.* p. 244). The naphthaquinone-monochlorimines are obtained from aminonaphthols and the dichloroimines from naphthylene diamines with bleaching powder (*Friedländer*, Ber. 27, 238). They resemble the benzoquinone-chlorimines, but do not give the colour reactions of the latter (*Friedländer*, *loc. cit.*). 1,4-Naphthaquinone-chlorimine,  $C_{10}H_7[1,4](NCl)O$ , m.p. 109°. 1,4-Naphthaquinone-dichlorimine,  $C_{10}H_6[1,4](NCl)_2$ , m.p. 137°.

1,2-Naphthaquinone-1-chlorimine, m.p. 87°, and 1,2-naphthaquinone-2-chlorimine, decomp. at 98°, are obtained from 2,1- and 1,2-aminonaphthol, and give 2,1-, and 1,2-nitrosonaphthol with hydroxylamine. 1,2-Naphthaquinone-dichlorimine, m.p. 105°.

4. NAPHTHAQUINONE-IMINES AND -ANILS. To this class belong the indophenol- and indoaniline-dyes of the naphthalene series (see p. 245), such as  $\alpha$ -naphthol-blue,  $C_{10}H_7[1]O[4]:N \cdot C_6H_4N(CH_3)_2$ , which is obtained from 1-naphthol and *as*-dimethyl-*p*-phenylene diamine or nitrosodimethylaniline. The simple 1,4-naphthaquinone-imine is not known, but a derivative of it, 2-amino-1,4-naphthaquinone-imine,  $C_{10}H_7[2]NH_2[1]O[4]NH$  (*Græbe*, Ann. 154, 303), is obtained by the oxidation of 1-hydroxy-2,4-diaminonaphthalene. When boiled with water it passes into 2-hydroxy-1,4-naphthaquinone-imine, m.p. 195° (*Kehrmann*, Ber. 23, 2454), and when treated with aniline it gives 2-amino-1,4-naphthaquinone-anil,  $C_{10}H_7[2]NH_2[1]O[4]NC_6H_5$ , m.p. 129°, and 2-anilino-1,4-naphthaquinone-anil,  $C_{10}H_7[2]NHC_6H_5[1]O[4]NC_6H_5$ , m.p. 187° (*Göes*, Ber. 13, 123; *Brönne*, Ber. 21, 391; *Fischer*, Ber. 21, 676; *Miller*, J. Russ. Phys.-Chem. Soc. 41, 1420). 2-Hydroxy-1,4-naphthaquinone-imine gives a monoxime with hydroxylamine, which occurs in two interconvertible forms, red and yellow in colour (*Kehrmann*, Ber. 29, 1415). 1,4-Naphthaquinone-anil,  $C_{10}H_7[1]O[4]NC_6H_5$ , red columns, m.p. 100°, and 1,2-naphthaquinone-2-anil,  $C_{10}H_7[1]O[2]NC_6H_5$ , m.p. 103°, dark-green needles, are obtained by the alkaline condensation of nitroso-benzene with 1- and 2-naphthol, respectively (*Euler*, Ber. 39, 1035). 2-Hydroxy-1,4-naphthaquinone-anil, m.p. 240° (decomp.), is obtained from 1,2-naphthaquinone-4-sulphonic acid, the oxidation product of 1,2-aminonaphthol-4-sulphonic acid, by the action of aniline in the cold. This is a case of transformation of a 1,2- into a 1,4-naphthaquinone derivative. *p*-Diamines react in a similar way to aniline, and in this way hydroxylated indo-aniline dyes can be obtained (*Böniger*, Ber. 27, 25, 3050). 1,4-Naphthaquinone-imine-anil,  $C_{10}H_7(NH)(NC_6H_5)$ , m.p. 129°, is obtained by oxidation of *p*-aminonaphthyl-phenylamine with mercuric oxide (*Fischer*, Ann. 286, 186).

1,2-Naphthaquinone-imines, also known as imino-oxo- or imino-keto-naphthalenes, such as  $C_{10}H_7[1,2]O(NH)$  (p. 623), are obtained by atmospheric oxidation of alkaline solutions of 1,2-aminonaphthols.

## 11. ALCOHOLS OF THE NAPHTHALENE SERIES AND THEIR OXIDATION PRODUCTS

A. ALCOHOLS. Naphthobenzyl alcohols, or naphthyl-carbinols,  $C_{10}H_7 \cdot CH_2OH$ , 1- m.p. 60°, b.p. 301°; 2- m.p. 80°, are obtained by the action of nitrous acid on the corresponding amines (*Bamberger*, Ber. 21, 257). The naphthobenzyl chlorides,  $C_{10}H_7CH_2Cl$ , 1- b.p. 178° (25 mm.), 2- m.p. 47°, are formed by the action of chlorine on the two methylnaphthalenes at the boiling point (*Scherler*,

Ber. 24, 3928). **Naphthobenzylamines**,  $C_{10}H_7CH_2NH_2$ , 1-b.p.  $292^\circ$ , 2-m.p.  $60^\circ$ , are prepared by the reduction of the corresponding thioamides of the naphthoic acids, and from the naphthonitriles. 1- and 2-Naphthyl-nitromethane,  $C_{10}H_7 \cdot CH_2NO_2$ , m.p.  $73^\circ$  and  $72^\circ$ , show similar tautomerism to phenylnitromethane (p. 256). They are obtained from the naphthyl-acetonitriles by the action of ethyl nitrate and sodium ethylate and fission of the nitroacetonitriles obtained by boiling with caustic soda (p. 256 and *Wislicenus*, Ber. 38, 508).

1-Naphthyl-dimethyl carbinol,  $C_{10}H_7C(OH)(CH_3)_2$ , m.p.  $80^\circ$ , is obtained from 1-naphthyl-methyl-ketone by the action of methyl magnesium iodide (see p. 606), and from 1-naphthylmagnesium bromide and acetone. 1-Naphthyl-phenyl carbinol,  $C_{10}H_7CH(OH)C_6H_5$ , m.p.  $86^\circ$ , and 1-Naphthyl-diphenyl carbinol,  $C_{10}H_7C(OH)(C_6H_5)_2$ , m.p.  $133^\circ$ , are obtained by the action of benzaldehyde and benzophenone, respectively, on 1-naphthyl-magnesium bromide (*Acree*, Ber. 37, 625, 2755). For further naphthyl-carbinols, see *Shurakowski*, J. Russ. Phys. Chem. Soc. 41, 1687.

**B. ALDEHYDES AND KETONES.** 1-Naphthaldehyde,  $C_{10}H_7CHO$ , b.p.  $291^\circ$ , and 2-naphthaldehyde, m.p.  $59^\circ$ , are obtained by oxidation of the naphthylcarbinols, or from 1- and 2-naphthyl-magnesium bromide, respectively (*Bamberger*, Ber. 20, 1115; *Brandis*, Ber. 22, 2148; *Straus*, Ann. 393, 227). 1-Naphthyl-acetaldehyde,  $C_{10}H_7 \cdot CH_2CHO$ , b.p.  $163-166^\circ$  (13 mm.), is obtained by the action of mercuric oxide on 1-vinyl-naphthalene (*Tiffeneau*, C.r. 147, 678). 1- and 2-Naphthyl-methyl-acetaldehyde,  $C_{10}H_7 \cdot CH(CH_3)CHO$ , b.p.  $132^\circ$  (4 mm.) and m.p.  $53^\circ$ , are obtained by the condensation of 1- and 2-naphthyl-methyl ketone with ethyl chloroacetate and sodium ethylate, with subsequent hydrolysis, and loss of carbon dioxide (*Darzens*, C.r. 145, 1342). The 1-compound has also been obtained by the action of mercuric oxide and iodine on 1-propenyl-naphthalene (*Tiffeneau*, C.r. 147, 678).

1- and 2-Naphthyl-methyl-ketone,  $C_{10}H_7COCH_3$ , 1-liquid, b.p.  $167^\circ$  (12 mm.), 2-m.p.  $51^\circ$ , b.p.  $172^\circ$  (11 mm.) (*Rousset*, Bull. [3], 15, 58), are obtained from naphthalene by the action of acetyl chloride in the presence of aluminium chloride, and have been separated by their picrates. The naphthyl-methyl-ketone chlorides lose HCl and give 1- and 2-naphthyl-acetylenes, which regenerate the ketones when treated with sulphuric acid. Oxidation of 1-naphthyl-methyl-ketone with permanganate gives 1-naphthyl-glyoxylic acid,  $C_{10}H_7 \cdot CO \cdot COOH$ , m.p.  $113^\circ$ , which can also be obtained by hydrolysis of naphthoyl cyanide, itself produced from naphthoyl chloride. 1-Naphthoyl-*o*-benzoic acid,  $C_{10}H_7COC_6H_4COOH$ , m.p.  $173^\circ$ , is obtained from phthalic anhydride, naphthalene, and aluminium chloride (*Gabriel*, Ber. 33, 448). Trialkyl-acetonaphthones are obtained by the action of sodamide and alkyl iodides on naphthyl-methyl-ketones (*Volmar*, C.r. 150, 1174). For other acyl-naphthyl-ketones, see *Bargellini*, Atti. Accad. Linc. Roma [5], 17, II, 26; for 2-hydroxy-6-acetonaphthalene, see *Fries*, Ber. 58, 2841. Phenyl-naphthyl-ketones, see *Caille*, Bull. [4], 3, 916; *de Fazi*, Gazz. 49, I, 242; *Willemari*, Ann. chim. [10], 12, 345.

1,4- and 2,1-Naphthol-aldehydes,  $C_{10}H_6(OH)CHO$ , m.p.  $181^\circ$ , and  $81^\circ$ , are best obtained by Gattermann's method (p. 265) in the form of their aldimines, by the action of hydrocyanic acid and hydrochloric acid on the naphthols in the presence of zinc chloride (*Gattermann*, Ber. 32, 284; cf. *Fosse*, Bull. [3], 25, 371). 1,2-Naphthol-aldehyde, m.p.  $59^\circ$ , is obtained by treating the condensation product of 1-naphthol and isatin chloride with caustic soda (*Bezdzik*, Mo. 29, 382; 30, 277). Naphthol-aldehyde-sulphonic acids are obtained by Reimer's synthesis by the action of chloroform and alkali on the naphthol-sulphonic acids (Ger. Pat. 97,934). 1-Naphthol-3-methyl-ketone,  $C_{10}H_6[1](OH)[3](COCH_3)$ , m.p.  $174^\circ$ , is produced by the condensation of 2-benzal-laevulinic acid (see p. 606 and *Erdmann*, Ber. 24, 3201). 1-Naphthol-4-methyl-ketone, m.p.  $198^\circ$ , is obtained from 1-naphthol-ethyl ether, acetyl chloride and aluminium chloride, with subsequent hydrolysis of the ethyl ether. Diacetonaphthol, m.p.  $140^\circ$ , is also produced. For other acetonaphthols, see *Witt*, Ber. 47, 3216. *peri*-Dihydroxy-naphthyl-ketones,  $(HO)_2[1,8]C_{10}H_6COR$ , obtained from *peri*-dihydroxynaphthalene by the action of carbon dioxide and zinc chloride are lake-forming mordant dyes (Ger. Pat. 126,199).

**C. NAPHTHALENE MONOCARBOXYLIC ACIDS.** 1-Naphthoic acid,  $C_{10}H_7COOH$ , m.p.  $160^\circ$ , is obtained: (1) by hydrolysis

of 1-naphthonitrile (*Bamberger*, Ber. 20, 242; *Ekstrand*, J. pr. [2], 38, 241); (2) by fusing 1-naphthalene sulphonic acid with sodium formate; (3a) by the action of magnesium and carbon dioxide on 1-bromonaphthalene in ether solution; (3b) by the action of ethyl chlorocarbonate and sodium on bromonaphthalene; (4) by the action of oxalyl chloride, or urea on naphthalene in the presence of aluminium chloride (*Gattermann*, Ber. 23, 1197; *Liebermann*, Ber. 44, 204). 2-Naphthoic acid, m.p. 182°, is obtained from 2-naphthonitrile (*Armstrong*, Proc. 1889, 122) and by oxidation of 2-alkylnaphthalenes (*Schulze*, Ber. 17, 1527; *Roux*, Ann. chim. phys. [6], 12, 289). Both acids lose carbon dioxide when heated with lime or baryta, and give naphthalene. The naphthoic acids are difficultly soluble in hot water.

*Homologous naphthalene carboxylic acids.*—1-Naphthyl-acetic acid,  $C_{10}H_7 \cdot CH_2 \cdot COOH$ , m.p. 131°; nitrile, b.p. 194° (18 mm.), has been obtained by the reduction of 1-naphthyl-glyoxylic acid (see above). The 2-acid, m.p. 139°; nitrile, m.p. 80°, is obtained from 2-naphthobenzyl chloride, through the cyanide (*Blank*, Ber. 29, 2373). 1- and 2-Naphthyl-acrylic acids,  $C_{10}H_7 \cdot CH \cdot CHCOOH$ , m.p. 205° and 196°, respectively, are obtained by Perkin's synthesis from the naphthol-aldehydes, sodium acetate, and acetic anhydride. With sodium propionate, the chief product is propenyl-naphthalene (p. 613), carbon dioxide being split off

(*Roussel*, Bull. [3], 17, 812). 1- and 2-Naphthocoumarin,  $C_{10}H_6 \begin{array}{l} \text{CH}=\text{CH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{array}$ ,

m.p. 141° and 118°, respectively, and their alkylated derivatives, are obtained by the general methods for preparing the coumarins (p. 472) by the action of malic acid, acetoacetic ester, etc., on naphthol in the presence of sulphuric acid, and from the naphthol-aldehydes by the Perkin synthesis (*Bartsch*, Ber. 36, 1966; *Knoevenagel*, Ber. 37, 4484; *Bezdzik*, Mo. 30, 280).

2-Phenyl- and 2-naphthyl-1-naphthoic acids are called *chrysenic* and *picenic* acids (see chrysene and picene, pp. 694, 702).

*Substituted naphthoic acids.*—By nitrating 1-naphthoic acid, 5- and 8-nitro-1-naphthoic acids, m.p. 239° and 275°, respectively, are obtained. On heating with nitric acid, they give 1,5(α-) and 1,8(β-) dinitronaphthalene (p. 614). 1,4-Nitronaphthoic acid, m.p. 220°, is obtained by the hydrolysis of its nitrile, which is obtained by treating the diazonium compound of 1,4-nitronaphthylamine with potassium cuprocyanide. By reduction with ferrous sulphate and ammonia, the 1,5-acid gives the stable 1,5-aminonaphthoic acid,  $C_{10}H_6(NH_2)COOH$ , m.p. 212° (*Ekstrand*, Ber. 19, 1982). 1,8- or *peri*-Aminonaphthoic acid, obtained from the 1,8-acid, like 1,8-aminosulphonic acid (p. 619), on the other hand, easily

gives an anhydride, the so-called naphthostyryl,  $C_{10}H_6 \begin{array}{l} [1]CO \\ | \\ (8)NH \end{array}$ , m.p. 179° (*Ek-*

*strand*, Ber. 19, 1131; *Bamberger*, Ber. 20, 242; *Schroeter*, Ber. 35, 4218). 1,4-Aminonaphthoic acid, m.p. 177° (*Friedländer*, Ber. 28, 1842). Nitration of 2-naphthoic acid gives rise to 5- and 8-nitro-2-naphthoic acid, and a little 1-nitro-2-naphthoic acid (*Ekstrand*, J. pr. [2], 43, 409; *Harrison*, J. 1926, 84). 2,3-Aminonaphthoic acid, m.p. 234°, has been obtained by the action of ammonia on the corresponding hydroxynaphthoic acid (*Mohlau*, Ber. 28, 3089). For other nitro- and amino-naphthoic acids, see *Friedländer*, C. 1899, I, 288. 1,3- and 1,4-Diamino-2-naphthoic acids, m.p. 85° and 185°, lose carbon dioxide and form 1,3- and 1,4-naphthylene-diamine. Their esters can be obtained by the nuclear synthetic method given on p. 607 (*Atkinson*, J. 91, 578; *Thorpe*, J. 91, 1004). 2,1- and 1,2-Aminonaphthoic acids, m.p. 126° and 205°, respectively, readily lose carbon dioxide forming the corresponding amines (*Friedländer*, Ber. 48, 328).

*Hydroxynaphthoic acids, naphthol-carboxylic acids*, which contain the OH- and COOH-groups in the ortho-position, are obtained like the *o*-phenol carboxylic acids (p. 355), by heating the sodium compounds of the naphthols with carbon

dioxide under pressure, or by heating the naphthols in toluene solution with sodium and carbon dioxide. 1,2-Naphthol-carboxylic acid,  $C_{10}H_8[1](OH)[2](COOH)$ , m.p. 191–192°, is obtained in this way from 1-naphthol. By the action of carbon dioxide on the sodium compound of 2-naphthol at 120°–145°, 2,1-naphthol-carboxylic acid, m.p. 158° (decomp.), is obtained. If the heating is carried to 200°–250°, 2,3-naphthol-carboxylic acid, m.p. 222–223°, is obtained. Ethers of 2-naphthol-carboxylic acid,  $AlkO[2]C_{10}H_7COOH$ , are obtained by the Grignard reaction from 1-bromo-2-naphthol-ethers, by the action of magnesium and carbon dioxide (*Bodroux*, *Bull.* [3], 31, 30). The 2,1-acid is characterised by the mobility of its carboxyl group. When heated by itself, or when boiled with water, it gives 1-naphthol, and with nitrous acid it gives 1-nitroso-2-naphthol (p. 632). With phenyl-diazonium salts it gives benzene-azo-2-naphthol, *etc.* The 2,3-acid, on the other hand, is very stable, and resembles salicylic acid. On account of its decided yellow colour, it has been proposed to give this acid the

formula corresponding to keto-dihydro-naphthoic acid,  $C_6H_7 \begin{matrix} \diagup CH_2-CO \\ \diagdown CH=CCOOH \end{matrix}$  (*Schöpf*, *Ber.* 29, 265; *Friedl*, *Mo.* 31, 917). The cause of the colour is, however, not clear (*cf.* *Lesser*, *Ber.* 58, 2109; *Fries*, *Ber.* 58, 2845).

1- and 2-Naphthol-carboxylic acids give the corresponding acid chlorides with thionyl chloride (*Zincke*, *Mo.* 22, 813). 2,3-Naphthol-carboxylic acid gives the colourless 2-chloro-3-naphthoic chloride, m.p. 56°, b.p. 248° (160 mm.) with phosphorus pentachloride (*Strohbach*, *Ber.* 34, 4158).

$\beta$ -Hydroxy-1,2- and 2,3-naphthocoumarin,  $C_{10}H_6 \begin{matrix} \diagup C(OH):CH \\ \diagdown O-CH \end{matrix}$ , m.p. 258° and 240°, respectively, are obtained from 1,2-naphtholcarboxylic chloride and acetyl-2,3-naphthol-carboxylic chloride by reaction with sodio-malonic ester, reacting in the same way as acetylsalicylic chloride (p. 485) (*Anschutz*, *Ann.* 367, 253; 368, 43).

All three *o*-naphthol-carboxylic acids give naphthoxanthenes

$C_{10}H_6 \begin{matrix} \diagup O \\ \diagdown CO \end{matrix} C_{10}H_6$ , when heated with acetic anhydride, (*Kostanecki*, *Ber.* 25, 1642).

1,4- and 1,5-Naphtholcarboxylic acids, m.p. 183–184° and 219°, respectively, are obtained from the corresponding naphthylamine-sulphonic acids by diazotisation, transformation into the cyanosulphonic acids, carboxyl-sulphonic acids, and finally fusion with potash (*Royle*, *J.* 123, 1641).

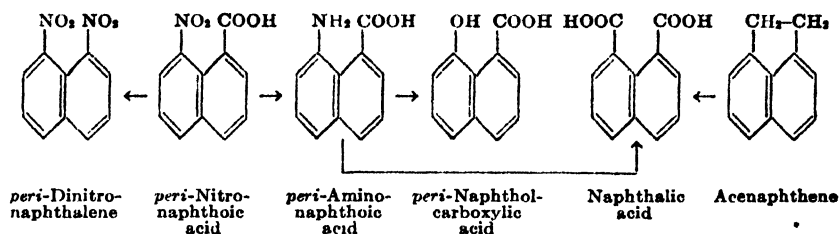
1,8- or *peri*-Naphtholcarboxylic acid is obtained by the decomposition of the diazonium compound of 1,8-amino-naphthoic acid, and like the latter, readily forms an anhydride, the  $\gamma$ -lactone,  $C_{10}H_6 \begin{matrix} \diagup [1]O \\ \diagdown [8]CO \end{matrix}$ , m.p. 169°.

2,3-Hydroxynaphthoic acid gives a mixed azo-compound with phenyldiazon-chloride, which on reduction breaks down to 1,2,3-amino-hydroxy-naphthoic acid. When boiled with sulphuric acid, this gives 1,2-dihydroxy-3-naphthoic acid, m.p. 215° (decomp.), which is also obtained from 1,2-sodio-naphthohydroquinone by the action of carbon dioxide, and is converted by oxidation into 1,2-naphthoquinone-3-carboxylic acid (*Mohlau*, *Ber.* 28, 3089). From 1,4-sodio-naphthohydroquinone and carbon dioxide, 1,4-dihydroxy-2-naphthoic acid, m.p. 186° (decomp.), is obtained, together with a condensation product of the acid belonging to the anthracene series (*Russig*, *J. pr.* [2], 62, 47). 1,3-Dihydroxy-2-naphthoic acid, or naphtho-resorcinol-carboxylic acid, m.p. 145° (decomp.), is obtained by the hydrolysis of its ethyl ester, m.p. 83°, which is itself obtained synthetically by the action of concentrated sulphuric acid on phenacetyl-malonic ester (p. 606) (*Metzner*, *Ann.* 298, 383). For other dihydroxy-naphthoic acids, see *Ber.* 29, 39.

The imides of the *o*-naphthoic-sulphonic acids are of interest as being the naphthalene analogues of saccharine. The three possible isomerides taste bitter and not sweet. They have been obtained from the naphthylamine sulphonic acids through the cyanosulphonic acids (*Kauffmann*, *Ber.* 55, 1499).

## D. NAPHTHALENE-DI- AND -POLY-CARBOXYLIC ACIDS.

Of the known naphthalene dicarboxylic acids, the most important is the 1,8- or *peri*-acid, called **naphthalic acid**,  $C_{10}H_6[1,8](COOH)_2$ , which is obtained by the oxidation of acenaphthene (p. 685), and by hydrolysis of its semi-nitrile, which is obtained from the diazonium compound of *peri*-aminonaphthoic acid. The following scheme shows the relationships of a series of *peri*-naphthalene derivatives:



Like the other *peri*-compounds of a similar kind (see above, and p. 626), naphthalic acid breaks down even on heating to  $180^\circ$ , without melting, into water and the anhydride,  $C_{10}H_6(CO)_2O$ , m.p.  $266^\circ$ . This is also readily formed by treating the acid with hydrochloric acid in alcohol, and by various other methods. Like phthalic anhydride, it condenses with phenol, giving phenolnaphthalein,

$C_{10}H_6 \begin{matrix} \text{C}(\text{C}_6\text{H}_4\text{OH})_2 \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{CO} \end{matrix}$  (Jaubert, Atti. r. acc. Lincei Rend. 1895, I, 392). With malonic ester and zinc chloride it gives *peri*-naphthindandione,

$C_{10}H_6 \begin{matrix} [1] \text{CO} \\ \diagup \quad \diagdown \\ [8] \text{CO} \end{matrix} \text{CH}_2$  (Errera, Gazz. 41, I, 190). For naphthanil and naphth-phenylhydrazil and other derivatives of naphthalic acid, see Jaubert, Ber. 28, 360; Anselm, Ber. 32, 3283; Grache, Ann. 327, 77; Francesconi, Gazz. 44, II, 92; Ostrogovich, Gazz. 41, II, 757.

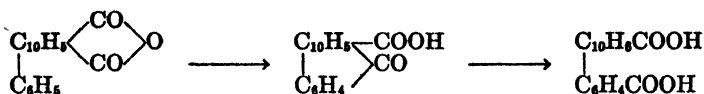
Naphthalimide,  $C_{10}H_6(CO)_2NH$ , m.p.  $300^\circ$ , gives naphthostyryl (p. 635) on treatment with sodium hypochlorite (Ullmann, Ber. 43, 440). Naphthalide,

$C_{10}H_6 \begin{matrix} [1] \text{CH}_2 \\ \diagup \quad \diagdown \\ [8] \text{CO} \end{matrix} \text{O}$ , m.p.  $160^\circ$ , may be regarded as a reduction product of naphthalic anhydride (Errera, Gazz. 44, II, 92).

Hydroxynaphthalic acids, see Dziewonski, Ber. 57, 1540. 1,2-Naphthalene-dicarboxylic acid, obtained by hydrolysis of its nitrile, melts at  $175^\circ$ , and is converted into its anhydride, m.p.  $105^\circ$  (Cleve, Ber. 25, 2475). 1,5-Naphthalene-dicarboxylic acid, see Moro, Gazz. 26, I, 89; Scholl, Ber. 55, 113. 1,4-Naphthalene-dicarboxylic acid, m.p.  $309^\circ$ , obtained by the hydrolysis of 1,4-dicyanonaphthalene, melts at  $309^\circ$  (Scholl, Ber. 55, 113); 1,7- and 2,3-naphthalene-dicarboxylic acids, m.p.  $265^\circ$  and  $246^\circ$ , respectively, see Ruzicka, Helv. 5, 923; Waldman, J. pr. [2], 128, 150. 1-Phenylnaphthalene-2,3-dicarboxylic acid,

$\text{C}_6\text{H}_5 \begin{matrix} \text{CH}=\text{CCOOH} \\ \diagup \quad \diagdown \\ \text{C}(\text{C}_6\text{H}_5)_2 \text{CCOOH} \end{matrix}$ , is obtained in the form of its anhydride, m.p.  $255^\circ$ , by heating phenyl-propionic acid,  $\text{C}_6\text{H}_5\text{C}::\text{CCOOH}$ , with acetic anhydride, a reaction recalling the formation of the aromatic ring from acetylenic compounds (pp. 478, 606).

It is also formed by illumination of a benzene solution of dibenzalsuccinic anhydride (p. 573). By the action of concentrated sulphuric acid, the colourless anhydride is converted into the allochrysoketo-carboxylic acid, m.p.  $288^\circ$ , which crystallises in mauve-red needles, and which on fusion with alkali passes into the isomeric 1-phenyl-naphthalene-dicarboxylic acid, m.p.  $288^\circ$  (Stobbe, Ber. 40, 3382; Pfeiffer, Ber. 40, 3839; Bucher, Am. 30, 1244):



1,4,5,8-Naphthalene-tetracarboxylic acid,  $\text{C}_{10}\text{H}_4[1,4,5,8](\text{COOH})_4$ , with the carboxyl groups in the two *peri*-positions, is obtained from pyrenic acid (p. 700) by oxidation (Bamberger, Ber. 20, 365; Freund, Ann. 399, 224; 402, 77).

**Naphthonitriles, or cyanonaphthalenes.**—The naphthonitriles are obtained by the distillation of the alkali metal salts of the naphthol sulphonic acids, or the phosphoric esters of the naphthols with potassium cyanide or potassium ferrocyanide, or from the naphthylamines through the diazonium compounds (Ekstrand, J. pr. [2], 38, 139, 271).

1-Naphthonitrile, or 1-cyanonaphthalene,  $\text{C}_{10}\text{H}_7\cdot\text{CN}$ , m.p.  $37^\circ$ , b.p.  $298^\circ$ , is obtained from 1-bromonaphthalene and potassium ferrocyanide (Merz, Ber. 10, 748). 2-Cyanonaphthalene, m.p.  $66^\circ$ , b.p.  $304^\circ$ . 1,2-Dicyanonaphthalene,  $\text{C}_{10}\text{H}_6(\text{CN})_2$ , m.p.  $190^\circ$ , is obtained by distilling 1,2-chloronaphthalene sulphonic acid with potassium ferrocyanide (Cleve, Ber. 25, 2475). 1,4-Dicyanonaphthalene, m.p.  $206^\circ$ . For other isomeric dicyanonaphthalenes, see Schaeffer, Ann. 152, 289; J. 1869, 483; Scholl, Ber. 55, 120). 1,4-Dicyano-2,3-dihydroxynaph-

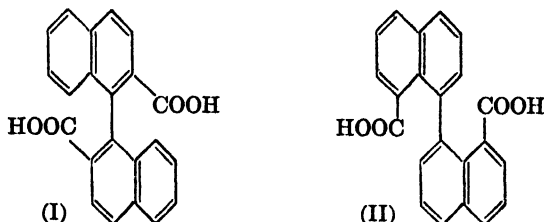
thalene,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{CN})\text{:COH} \\ | \\ \text{C}(\text{CN})\text{:COH} \end{array}$ , m.p.  $291^\circ$ , is obtained synthetically by the condensation of ethyl oxalate and *o*-xylylene cyanide (p. 606).

#### (b) Dinaphthyl, Dinaphthylmethane, and Trinaphthylmethane Derivatives

Various isomeric **dinaphthyls** have been obtained by passing naphthalene vapour through red-hot tubes, by heating naphthalene with aluminium chloride, by the action of sodium or copper bronze on bromo- and iodo-naphthalene, by heating mercury dinaphthyl,  $\text{Hg}(\text{C}_{10}\text{H}_7)_2$  (Chattaway, J. 65, 877), etc. 1,1'-Dinaphthyl, m.p.  $157^\circ$ , gives perylene,  $\text{C}_{10}\text{H}_6 \left\{ \begin{array}{c} [1] \\ [8] \end{array} \right\} \text{C}_{10}\text{H}_6$ , on heating with aluminium chloride to  $140^\circ$ . By nitration, 4-, and 4,4'-mono- and di-nitro-1,1'-dinaphthyl are formed (Burton, Am. 45, 1566). The compounds corresponding to benzidine or 4,4'-diaminodiphenylene, viz., 4,4'-diamino-1,1'-dinaphthyls, or naphthidines, are obtained, together with 1,1'-diamino-2,2'-dinaphthyls or dinaphthylines, by the transformation of the hydrazonaphthalenes (p. 618), or directly from the naphthylamines by the action of 80% sulphuric acid in the presence of oxidising agents, such as ferric chloride, etc. (Reverdin, Ch.-Ztg. 16, 1687). By the action of ferric chloride on the naphthols, **dinaphthols** are formed, which can also be obtained from the naphthidines through the diazo-compounds, or by the action of copper powder on the halogeno-naphthols. 2,2'-Dihydroxy-1,1'-dinaphthyl ( $\beta$ -dinaphthol), m.p.  $216^\circ$ . **Halogeno-dinaphthyls**, see Corbellini, Gazz. 59, 301. 3,3'-Diamino-1,1'-dinaphthyl, m.p.  $270^\circ$ . 4,4'-Diamino-1,1'-dinaphthyl, or naphthidine, m.p.  $202^\circ$  and other compounds of this type, see Cumming, J. 1932, 528. For optically active azo-dyes obtained from these compounds, see Murashiki, Sci. Papers Inst. Phys. Chem. Res. 17, 297. For binuclear quinones of the dinaphthyl series, see Russig, J. pr. [2], 64, 31; Friedländer, Ber. 42, 1058. For free radicals with naphthyl residues, see Vol. IV.

**MOLECULAR ASYMMETRY OF OPTICALLY ACTIVE DINAPHTHYL DERIVATIVES.** As in the case of *o*-substituted diphenyl- and triphenyl-derivatives (pp. 506, 508), 2,2'- or 8,8'-substituted dinaphthyl derivatives show optical activity although there is no asymmetric carbon atom. Thus, 1,1'-dinaphthyl-2,2'-dicarboxylic acid (I) (Kuhn, Ann. 465, 282) and 1,1'-dinaphthyl-8,8'-dicarboxylic acid (II) (Kalb, Ber. 47, 1728) have been resolved, the former by means of quinine and the latter with brucine. The

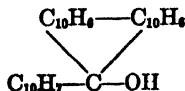
cause of this spatial isomerism is the same as with the diphenyl derivatives (see p. 506).



Dinaphthylmethanes and their derivatives are obtained by similar methods to those adopted for obtaining the corresponding compounds in the diphenylmethane series (p. 510). 1,1'- and 2,2'-Dinaphthylmethane,  $\text{CH}_2(\text{C}_{10}\text{H}_7)_2$ , m.p.  $109^\circ$  and  $92^\circ$ , respectively. 1,2-Dinaphthylmethane, m.p.  $96^\circ$ , see *Tshitshibabin*, Ber. 44, 449. 1,1',1'-Trinaphthylmethane is unstable (*Tshitshibabin*, J. pr. [2], 84, 760). 2,2',2''-Trinaphthylmethane, m.p.  $178-179^\circ$ , is obtained by reduction of the carbinol with hydriodic acid in glacial acetic acid (*Tshitshibabin*, J. pr. [2], 88, 505, 512). Trichloroethylidene-1,1'-dinaphthyl,  $\text{CCl}_3\text{CH}(\text{C}_{10}\text{H}_7)_2$ , m.p.  $156^\circ$ , gives on warming with zinc dust and alcohol, 1,1'-naphthostilbene,  $\text{C}_{10}\text{H}_7\text{CH}:\text{CHC}_{10}\text{H}_7$ , m.p.  $161^\circ$ . This compound is closely related to piceic (p. 702) into which it passes on strongly heating. 2,2'-Naphthostilbene, m.p.  $255^\circ$  (*Wislicenus*, Ber. 38, 509). Alkylidene-dinaphthylamines are very easily formed from naphthylamines and alcohols, and alkylidene-naphthols from naphthols and aldehydes (*Morgan*, J. 77, 814, etc.). The products obtained from aldehydes and 2-naphthols readily split off water and pass into xanthenes. They must therefore contain the alkylidene groups in the *o*-position to the hydroxyls. 2,2'-dinaphthol-

methane, m.p.  $194^\circ$ , gives dinaphthoxanthene,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{C}_{10}\text{H}_6$ , on treatment with phosphorus oxychloride. Benzaldehyde and 2-naphthol give an acetal and *ms*-phenylnaphthoxanthene,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_{10}\text{H}_6)_2$ , (*Abel*, Ber. 25, 3477; *Wolff*, Ber. 26, 83). By the action of chloroform on sodio-2-naphthol at  $150^\circ$ , an anhydride of trihydroxy-trinaphthylmethane,  $\text{HOC}_{10}\text{H}_6\text{CH}(\text{C}_{10}\text{H}_6)_2\text{O}$ , m.p.  $273^\circ$ , is obtained. This compound is also formed by condensation of 2-naphthol with 2-naphthol-aldehyde (*Fosse*, C.r. 132, 787; Bull. [3], 25, 371).

1,1'- and 2,2'-Dinaphthylcarbinol,  $(\text{C}_{10}\text{H}_7)_2\text{CHOH}$ , m.p.  $146-147^\circ$ , are obtained from 1- and 2-naphthyl-magnesium bromide and ethyl formate. When oxidised they give 1,1'-dinaphthylketone and 2,2'-dinaphthylketone, m.p.  $98^\circ$  and  $164^\circ$ , respectively. 1,2'-Dinaphthylketone, m.p.  $135^\circ$  (*Tshitshibabin*, J. pr. [2], 88, 505). The corresponding chlorides,  $(\text{C}_{10}\text{H}_7)_2\text{CHCl}$ , are readily obtained by the action of hydrochloric acid, and from these, by the action of magnesium and carbon dioxide, 1,1'- and 2,2'-dinaphthylacetic acid,  $(\text{C}_{10}\text{H}_7)_2\text{CHCOOH}$ , m.p.  $228^\circ$  and  $179^\circ$ , have been obtained. When treated with zinc and hydrochloric acid the dinaphthylcarbinols readily lose water and pass into 1,1'- and 2,2'-dibenzofluorene (p. 684) (*Schmidlin*, Ber. 42, 2377, 2392; 43, 2824). 1,1',1'-Trinaphthylcarbinol, m.p.  $160-180^\circ$ , is obtained by the action of 1-naphthyl magnesium bromide on 1,1'-dinaphthylketone. It combines with ether and benzene forming molecular compounds, and is oxidised in the air to 1-naphthyl-dibenzofluorenol:



(*Tshitshibabin*, J. pr. [2], 84, 769). 2,2',2''-Trinaphthylcarbinol, m.p.  $204^\circ$ , is not autoxidisable, but readily loses water, giving 2-naphthyl-2-dibenzofluorene (*Tshitshibabin*, J. pr. [2], 88, 510).

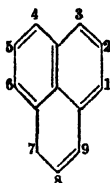


A large number of dyes of the naphthyldiphenyl-, dinaphthylphenyl-, and trinaphthyl-methane series have been prepared by the usual methods. They are of no practical interest (*Noelling*, Ber. 37, 1899).

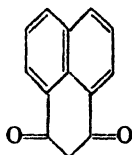
**Tetra-1-naphthylethane**, m.p. 277°, is obtained in small yield from 1-dinaphthylcarbinol by the action of zinc and glacial acetic acid. **Tetranaphthylethylene**, m.p. 322°, is formed when 1-dinaphthylcarbinol is treated with phosphoric acid (*Tshitshibabin*, J. Russ. Phys.-Chem. Soc. 46, 1389).

By the introduction of a six-membered ring into the *peri*-position of naphthalene, *peri*-benzonaphthalene, or benznaphthene, or phenaline, is formed (I).

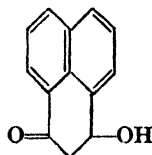
The following of its derivatives are of importance. **7,9-Diketo-8,9-dihydro-*peri*-benznaphthene**, or *peri*-naphthindandione (II), is obtained by the action of naphthalic anhydride on diethyl malonate and heating with zinc chloride to 170–175°. It forms yellowish-red crystals, melting at 265° with decomposition, and appears to exist chiefly in the tautomeric form (III) (*Tshitshibabin*, Ber. 44, 1105; *Errera*, Gazz. 41, II, 807). By reduction with hydriodic acid and phosphorus, and subsequent dehydrogenation, it forms **dihydro-benzonaphthalene**, or *peri*-naphthindane (IV), m.p. 68–69°:



(I)

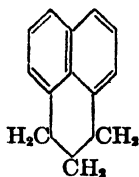


(II)

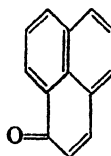


(III)

**Pyrene-ketone**,  $C_{12}H_8(CO)$  (V), m.p. 141°, also belongs to this series of compounds. It is formed by distillation of pyrenic acid (p. 700), with slaked lime (*Bamberger*, Ber. 19, 1997; Ann. 240, 178):



(IV)



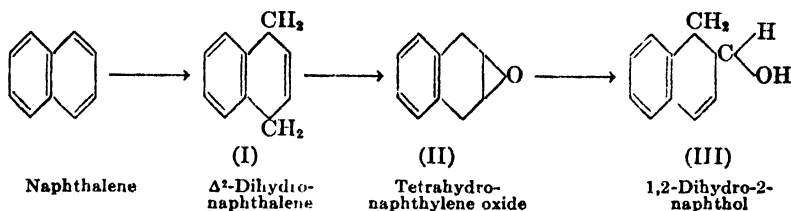
(V)

### (c) Hydronaphthalene Compounds

Just as cyclohexane derivatives are formed by the hydrogenation of the aromatic ring system in benzene, hydroaromatic compounds, known as hydronaphthalenes, are obtained by hydrogenation of naphthalene. The less marked aromatic character of naphthalene compared with benzene is evident in the fact that the addition of hydrogen (or halogen) takes place more easily in the case of naphthalene than with benzene derivatives. According to the conditions, dihydro-, tetrahydro-, or finally decahydro-naphthalenes can be obtained. In the following paragraphs, dihydro- and tetrahydro-

**naphthalenes**, which still contain one benzene ring intact, will be described. For hexa-, octa-, and deca-hydronaphthalenes, see Vol. II, p. 170.

**A. DERIVATIVES OF DIHYDRONAPHTHALENE.** By reduction of naphthalene with sodium and alcohol at the boiling point, 1,4- or  $\Delta^2$ -dihydronaphthalene, or 1,4-dialine (I),  $C_{10}H_{10}$ , m.p.  $25^\circ$ , b.p.  $94.5^\circ$  (17 mm.), is obtained. The fact that the two additional hydrogen atoms are in the 1,4-position is shown by oxidation to *o*-phenylene-diacetic acid. 1,4-Dialine is to be regarded as the parent hydrocarbon of 1,4-naphthaquinone. It is similar to the olefines, *e.g.*, ethylene, in the fact that it readily adds on two monovalent atoms or radicals. With bromine it gives a dibromide, m.p.  $71.5-72^\circ$ , and with HOCl it gives a glycol-chlorhydrin (see p. 643). Tetrahydronaphthylene oxide (II), which is readily obtained from the latter (p. 643), will isomerise into 1,2-dihydro-2-naphthol,  $C_{10}H_{10}O$  (III), b.p.  $162-168^\circ$  (28 mm.), which on oxidation gives dihydro-isocoumarin-carboxylic acid, and on loss of hydrogen gives naphthalene (*Bamberger*, Ann. 288, 74).



1-Phenyl- $\Delta^2$ -dihydronaphthalene,  $C_6H_5 \cdot \begin{array}{c} \text{CH}(C_6H_5) \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \quad \text{CH} \end{array}$ , m.p.  $50^\circ$ , is obtained by boiling 1-phenyl-2-bromo-tetrahydronaphthoic acid-3 (p. 645) with caustic soda, or better diethyl-aniline (*Thiele*, Ann. 306, 235).

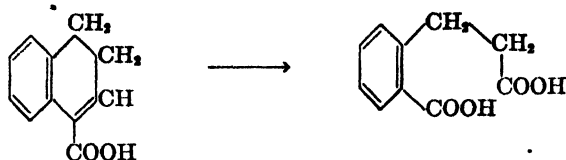
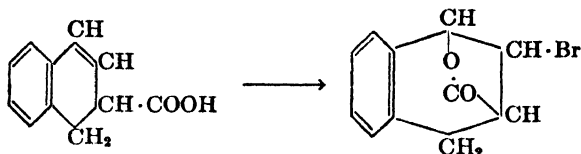
**Naphthalene dichloride**,  $C_{10}H_8Cl_2$ , obtained by the action of hydrochloric acid and potassium chlorate on naphthalene, is a yellowish oil, which splits off hydrogen chloride even at  $40-50^\circ$ , forming 1-chloronaphthalene.

1,2- or  $\Delta^1$ -Dihydronaphthalene, 1,2-dialine, m.p.  $-7^\circ$ , b.p.  $78^\circ$  (9 mm.), is obtained from the  $\Delta^2$ -isomeride, by isomerisation with sodium ethylate, or by treating 1,2-dibromo-tetraline, m.p.  $71-72^\circ$ , with magnesium (*Straus*, Ber. 46, 236; *Willstätter*, Ber. 46, 531; *Straus*, Ber. 54, 25; *von Braun*, Ber. 54, 597).

5,8- and 5,6- (or 7,8?)-Dihydro-1-naphthylamine, m.p.  $37.5^\circ$ , b.p.  $247^\circ$  (40 mm.) and b.p.  $180-182^\circ$  (30 mm.), respectively, are obtained by the reduction of 1-naphthylamine with sodium, and can be separated by the benzyldiene compounds (*Rowe*, J. 117, 1574). In the same way, 5,8- and 5,6- (or 7,8?)-dihydro-1-naphthol, m.p.  $71^\circ$  and  $75^\circ$ , can be obtained from 1-naphthol. The 5,8- and 5,6- (or 7,8?)-compounds isomerise on heating to  $125^\circ$  in alkaline solution. They are also obtained from the corresponding amino-compounds by diazotisation and boiling. For derivatives, see *Rowe*, J. 119, 2021.

**DIHYDRONAPHTHOIC ACIDS.** When 1- and 2-naphthoic acids are reduced with sodium amalgam, two H-atoms are taken up in the ring containing the carboxyl group, and in the cold labile,  $\beta, \gamma$ -unsaturated-, and in the warm, stable  $\alpha, \beta$ -unsaturated dihydronaphthoic acids,  $C_{10}H_7 \cdot COOH$ , are formed.  $\Delta^1$ -1- is stable, m.p.  $121^\circ$ ;  $\Delta^2$ -1- is labile, m.p.  $86-87^\circ$ ;  $\Delta^2$ -2- is stable, m.p.  $162-163^\circ$ , and  $\Delta^2$ -2- is labile, m.p.  $101^\circ$ .  $\Delta^1$ -Dihydro-2-naphthoic acid, is obtained from  $\alpha$ -hydroxymethylene- $\gamma$ -phenyl-butyric ester by the action of concentrated sulphuric acid (*Auwers*, J. pr. [2], 109, 124).

By boiling with sodium hydroxide solution, the unstable forms are converted into the stable ones. The stable 1-acid gives hydrocinnamic acid when oxidised with permanganate, but the unstable acid gives oxalic and phthalic acids. The dibromide of the unstable 2-acid readily gives a brominated lactone, whereas the stable form does not. From these facts the following formulae for the stable 1- and the unstable 2- acids have been deduced (*Baeyer*, Ann. 266, 169):

Stable dihydronaphthoic acid ( $\Delta^1$ , 1)Unstable dihydronaphthoic acid ( $\Delta^2$ , 2)

Dihydro-2-naphthoic acids are oxidised by potassium ferricyanide to 2-naphthoic acid. The stable 1-dihydronaphthoic acid, like other  $\alpha, \beta$ -unsaturated carboxylic acids, in the form of its ester adds on sodio-acetoacetic ester, and forms a  $\Delta$ -ketonic acid ester. This splits off alcohol and condenses further to a hydrogenated derivative of phenanthrene (p. 669) (*Rabe*, Ber. 31, 1896).

1-Phenyl-dihydro-2-naphthoic acid,  $C_{10}H_8(C_6H_5)COOH$ , m.p.  $191^\circ$ , is obtained by the condensation of dibenzal-propionic acid (p. 584) with a mixture of glacial acetic and sulphuric acids (*Thiele*, Ann. 306, 156).

**B. TETRAHYDRONAPHTHALENE DERIVATIVES.** Tetrahydronaphthalene, or *tetraline*,  $C_{10}H_{12}$ , m.p.  $-30^\circ$ , to  $-27^\circ$ , b.p.  $206-208^\circ$ , is obtained by the reduction of naphthalene with sodium and amyl alcohol, hydriodic acid and phosphorus, or hydrogen and finely divided nickel at  $190^\circ$ . If the naphthalene is poisoned by treatment with an alkali metal, it can also be hydrogenated with a platinum catalyst and hydrogen (*Schroeter*, Ann. 426, 1). According to the oxygen-content of the catalyst used, the hydrogenation proceeds to the tetrahydro- or direct to the decahydronaphthalene (see Vol. II, p. 171) (*Willstätter*, Ber. 56, 1388). Tetraline is also formed from *ar*-tetrahydronaphthylamine by elimination of the  $NH_2$  group.

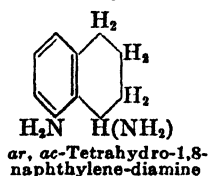
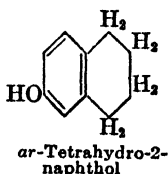
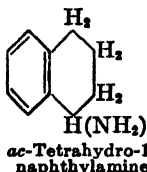
Naphthalene tetrachloride,  $C_{10}H_8Cl_4$ , m.p.  $182^\circ$ , is obtained by passing a current of chlorine into a chloroform solution of naphthalene; when boiled with alcoholic potash it gives dichloronaphthalene (p. 614). For the oxidation of naphthalene tetrachloride, see *Helbig*, Ber. 28, 505. For chlorine addition products of chlorinated and sulphonated naphthalenes, see *Armstrong*, Proc. 1890, 85. Naphthalene tetrabromide, m.p.  $111^\circ$  (*Orndorff*, Am. Chem. J. 19, 262).

Nitration of tetraline at  $0^\circ$  leads to the formation of a mixture of equal parts of *ar*-1-nitrotetraline, m.p.  $34^\circ$ , and *ar*-2-nitrotetraline, m.p.  $31.5^\circ$ . Under more energetic conditions, *ar*-1,2- and -1,3-dinitrotetraline, m.p.  $103^\circ$  and  $95^\circ$ , and finally *ar*-1,2,4-trinitrotetraline, m.p.  $95^\circ$ , are obtained.

When *ar*-1-nitrotetraline is reduced with zinc and alkali, *ar*-1,1'-azoxy-, -azo-, and -hydrazo-tetraline, are obtained in straw-yellow, red, and colourless needles, respectively, and melting at  $184^\circ$ ,  $191^\circ$ , and  $183^\circ$ , respectively. Hydrazo-tetraline undergoes the benzidine transformation and gives tetralidine, *ar*-4,4'-diamino-1,1'-ditetralyl, m.p.  $153-154^\circ$ . After tetra-diazotisation it couples with the usual dye components giving substantive cotton dyes (*Schroeter*, Ann. 426, 19).

The tetrahydro-derivatives of the naphthylamines and naphthols are of special importance. They are obtained by treatment with sodium and amyl alcohol at the boiling point, or by catalytic reduction. Four H-atoms are taken up in one nucleus. Some of the tetrahydro-naphthylamines can be obtained by the catalytic reduction of nitrotetralines. *ar*-1-Nitrotetraline can be reduced by sodium sulphide (*Vesely*, Rec. 44, 352). If the hydrogenated nucleus is the one bearing the  $NH_2$  or OH group, the derivative concerned loses the character of a naphthylamine or a naphthol, and behaves as if these groups were substituted in the side-chain. If the non-substituted nucleus is hydrogenated, the substances retain the

characteristics of homologous anilines or phenols. The latter are therefore called aromatic (*ar*-) and the former aliphatic-cyclic or alicyclic (*ac*-) compounds:



1-Naphthylamine and 1-naphthol give *ar*-tetrahydro-1-naphthylamine and -1-naphthol on reduction, but the 2-compounds give the *ac*-tetrahydro derivatives in addition to the *ar*-, the former predominating. 1,8-Naphthylene-diamine gives *ac*-, *ar*-tetrahydronaphthylene-diamine, which gives *ac*-tetrahydro-1-naphthylamine on replacement of the  $\text{NH}_2$  by H.

**ar-Tetrahydro-naphthylamines**,  $\text{NH}_2 \cdot \text{C}_6\text{H}_7$ : ( $\text{C}_{10}\text{H}_9$ ), 1- b.p.  $275^\circ$ , 2- b.p.  $276^\circ$ , are weak bases, which form diazo- and azo-compounds. They readily reduce the salts of the noble metals. When oxidised by permanganate they give oxalic and adipic acids. When oxidised with chromic acid, the 1-compound gives *ar*-tetrahydro-1,4-naphthaquinone,  $\text{C}_8\text{H}_6\text{O}_2$ : ( $\text{C}_8\text{H}_6$ ), m.p.  $55^\circ$ , which strongly resembles benzoquinone, and possesses stronger oxidising powers than 1,4-naphthaquinone. **ac-Tetrahydronaphthylamines**,  $\text{C}_6\text{H}_7$ : ( $\text{C}_6\text{H}_7 \cdot \text{NH}_2$ ), 1- b.p.  $246^\circ$ , 2- b.p.  $249^\circ$ , are strong bases, which absorb carbon dioxide from the air. Oxidation with permanganate opens only the hydrogenated ring, forming hydrocinamic-*o*-carboxylic acid. From 2, *ac*-tetrahydronaphthylamine an optically active dextro-rotatory modification has been obtained by means of *d*-bromocamphor sulphonie acid (Pope, Proc. 15, 170; 16, 74). It increases blood pressure and raises the body temperature (von Braun, Ber. 55, 3664). **ac**-, **ar**-**Tetrahydro-1,5-naphthylene diamine**,  $\text{H}_2\text{N} \cdot \text{C}_6\text{H}_7$ : ( $\text{C}_6\text{H}_7 \cdot \text{NH}_2$ ), m.p.  $77^\circ$ , b.p.  $264^\circ$ , combines the properties of an aromatic and an alicyclic amine. It has been resolved into a dextro- and laevo-rotatory form.

**Tetrahydronaphthols**, or *tetralols*, are obtained by the reduction of naphthols and by fusion of the corresponding sulphonie acids with alkali, or by the action of nitrous acid on the tetrahydronaphthylamines (Schroeter, Ann. 426, 90; Brochet, C.r. 172, 1499). **ac-Tetrahydro-1-naphthol**,  $\text{C}_6\text{H}_7$ : ( $\text{C}_6\text{H}_7\text{OH}$ ), b.p.  $139$ – $140^\circ$ , and **ac-tetrahydro-2-naphthol**, b.p.  $144$ – $146^\circ$  (20 mm.), behave like aliphatic alcohols, and resemble the similarly constituted terpene-alcohols, menthol and borneol (Vol. II, pp. 216, 217). **ar-Tetrahydro-1-naphthol**,  $\text{HO} \cdot \text{C}_6\text{H}_7$ : ( $\text{C}_6\text{H}_8$ ), m.p.  $69^\circ$ , b.p.  $265^\circ$ , and **ar-tetrahydro-2-naphthol**, m.p.  $57.5^\circ$ , behave like homologous naphthols. For derivatives of the tetralols, see Schroeter, Ann. 426, 90, and Thoms, Ar. Pharm. 265, 336.

Sulphonation of tetraline leads to **ar-tetraline-2-sulphonic acid**, m.p.  $75^\circ$ . By the action of chlorosulphonic acid on tetraline, **ar**-2- and -1-tetraline-sulphonyl chlorides are obtained, and the free sulphonic acids can be obtained from them by hydrolysis. **ar-Tetraline-1-sulphonic acid**, m.p.  $110^\circ$  (Schroeter, Ann. 426, 83).

A series of tetrahydro-naphthalene derivatives have been obtained from dihydronaphthalene. Phenol adds on to dihydronaphthol forming **tetrahydro-naphthylphenol**,  $\text{C}_8\text{H}_7$ : ( $\text{C}_8\text{H}_7 \cdot \text{C}_6\text{H}_5\text{OH}$ ), m.p.  $130^\circ$  (Koenigs, Ber. 24, 179), and bromine adds on to give dihydronaphthalene dibromide,  $\text{C}_8\text{H}_6$ : ( $\text{C}_8\text{H}_6\text{Br}_2$ ). When boiled with potassium carbonate, or by the action of silver acetate followed by hydrolysis, this gives **ac-tetrahydronaphthalene-(2,3)-diol**,  $\text{C}_8\text{H}_8$ :

$$\begin{array}{c} \text{CH}_2 - \text{CH} \cdot \text{OH} \\ | \\ \text{CH}_2 - \text{CH} \cdot \text{OH} \end{array}$$

*trans*-form m.p.  $135^\circ$ , *cis*-form m.p.  $120^\circ$  (Bösesken, Rec. 40, 519). This compound breaks down on oxidation to *o*-phenylene-diacetic acid. It is an analogue of ethylene glycol; the chlorhydrin,  $\text{C}_{10}\text{H}_{10}\text{Cl}(\text{OH})$ , m.p.  $117^\circ$ , gives **tetrahydro-naphthylene-2,3-oxide**,  $\text{C}_{10}\text{H}_{10}\text{O}$ , m.p.  $43^\circ$ , b.p.  $258^\circ$ , with alkali. This compound shows all the properties of ethylene oxide. A series of "alkines" have been prepared by the action of bases on the chlorhydrin. Of these, **hydroxytetrahydro-**

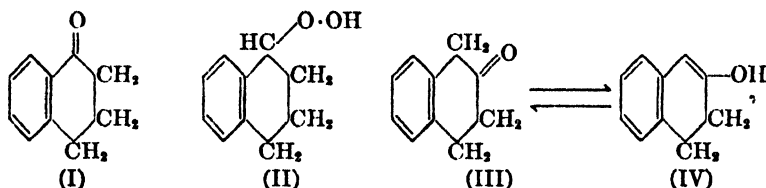
**naphthylene-trimethyl-ammonium hydroxide**,  $\text{C}_8\text{H}_8$ :

$$\begin{array}{c} \text{CH}_2 - \text{CHOH} \\ | \\ \text{CH}_2 - \text{CH} \cdot \text{N}(\text{CH}_3) \cdot \text{OH} \end{array}$$

should be mentioned, because of its connection with choline (*cf.* Vol. I, p. 379).

**ac-Tetrahydronaphthalene-(1,2)-diol**, *cis*-form m.p. 102°, *trans*-form m.p. 112–113°, is obtained by the oxidation of  $\Delta^3$ -dihydro-naphthalene (p. 641) with mercuric acetate (Böeseke, *Rec.* 40, 519). For derivatives, see *Straus*, *Ber.* 54, 40.

**$\alpha$ -Tetralone**, 1-keto-tetrahydro-naphthalene (I) is formed by passing oxygen into tetraline in the presence of a mixture of lead, cobalt, and manganese oleates at 65° (*Ger. Pat.* 568,338), or by the action of alkali on the peroxide (II),

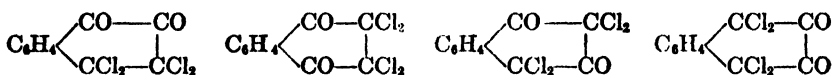


m.p. 56°, which is formed from tetraline on treatment with air or oxygen, and on reduction with zinc dust is converted into *ac*- $\alpha$ -tetralol (*Hartmann*, *Helv.* 15, 1390; *Bergmann*, *Ber.* 66, 51).  $\alpha$ -Tetralone can also be prepared by intramolecular condensation of  $\gamma$ -phenyl-butyryl chloride (p. 295) with aluminium chloride (*Kipping*, *J.* 75, 144; *Mayer*, *Ber.* 56, 1424).

**$\beta$ -Tetralone**, 2-keto-tetrahydronaphthalene (III), m.p. 18°, b.p. 138° (16 mm.), can be obtained by the action of weak alkalis on the chlorohydrin of tetrahydronaphthalene-2,3-diol, or by distillation of *o*-phenylene-propiono-acetic acid (p. 395) (*Einhorn*, *Ann.* 286, 257). It reacts like a ketone towards sodium bisulphite, phenylhydrazine, and hydroxylamine (*Bamberger*, *Ber.* 27, 1547), but, on the other hand, also shows the properties of an enol, so that it can also be regarded as the tautomeric *ac*-(3,4)-dihydro-2-naphthol (IV) (*Straus*, *Ber.* 54, 40; *von Braun*, *Ber.* 55, 3661).

***ac*-2-Hydroxy- $\alpha$ -tetralone**, m.p. 36°, obtained from bromotetralone through the acetate, is unstable, and passes into 2-naphthol under the influence of acids. In alkaline solution it undergoes autoxidation, which gives 2-hydroxy-1,4-naphthaquinone, with intermediate formation of dimers (*Straus*, *Ann.* 444, 165).

**DIKETOTETRAHYDRONAPHTHALENES** have been obtained in the form of their chloro-derivatives by the action of chlorine on the corresponding dihydroxynaphthalenes or naphthaquinones (p. 631) (*Zincke*, *Ann.* 300, 180; 334, 342):



**Diketotetrahydronaphthylene oxide**,  $C_6H_4$  m.p. 136°, is obtained by the action of bleaching powder on 1,4-naphthaquinone (p. 631 and *Zincke*, *Ann.* 286, 71).

***ar*-Tetrahydronaphthalene-1-aldehyde**, b.p. 135° (18 mm.), and **-2-aldehyde**, b.p. 150–155° (14 mm.), have been obtained by the oxidation of the corresponding methyl-tetralines with chromyl chloride (*Fleischer*, *Ber.* 55, 3290). ***ar*-Tetrahydronaphthyl-2-methyl ketone**,  $CH_3 \cdot CO \cdot C_6H_3$  ( $C_6H_3$ ), b.p. 182°, is obtained from tetraline, acetyl chloride, and aluminium chloride (*von Braun*, *Ber.* 55, 1687).

**Tetrahydronaphthoic acids** can also be distinguished as aromatic and alicyclic. ***ar*-Tetrahydro-1-naphthoic acid**,  $HOOC \cdot C_6H_3$  ( $C_6H_3$ ), *amide*, m.p. 182°, is obtained from the nitrile, which is obtained by the action of potassium cyanide and cuprous cyanide on tetrahydro-1-naphthalene diazonium chloride. ***ar*-Tetrahydro-2-naphthoic acid**, m.p. 152–153°, has been obtained by reduction of 2-naphthoic acid with hydrogen in the presence of nickel oxide, under pressure (*Ipatiev*, *Ber.* 42, 2101). It can also be obtained by the action of oxalyl chloride on tetraline (*von Braun*, *Ber.* 53, 1161).

***ac*-Tetrahydronaphthoic acids**, 1- m.p. 85°, 2- m.p. 96°, are obtained by the

reduction of naphthoic and dihydronaphthoic acids with sodium amalgam. They are more stable towards permanganate than the dihydro-acids, behaving as saturated acids. By longer action of oxidising agents they are converted into phthalic and oxalic acids (*Baeyer*, Ann. 266, 202). For the resolution of the tetrahydronaphthoic acids into their optically active components, see *Pickard*, Proc. 22, 2021; J. 89, 1101. *ac*-Phenyltetrahydro-2-naphthoic acid,  $[C_6H_5(C_6H_4)COOH]$ , m.p. 177°, is obtained by the reduction of phenylbromo-tetrahydronaphthoic acid, m.p. 205°, which is obtained synthetically by the action of bromine at 0° on a chloroform solution of benzyl-phenyl-isocrotonic acid (p. 585) (*Thiele*, Ann. 306, 231).

*ac*-Tetrahydronaphthalene-2,2-dicarboxylic acid,  $C_{10}H_6[C_6H_5(COOH)_2]$ , melts at 199°, with formation of the anhydride, m.p. 184°. The latter is obtained by heating the potassium salt of tetrahydronaphthalene-tetracarboxylic acid, of which the ester can be obtained synthetically by the action of sodio-malonic ester on *o*-xylylene dibromide (p. 606) (*Baeyer*, Ber. 17, 448). Tetrahydro-1, 5-naphthalene dicarboxylic acid, m.p. 238° (*Moro*, Gazz. 26, I, 89).

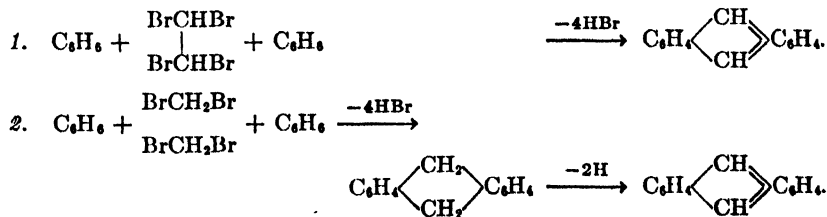
### 3. ANTHRACENE GROUP

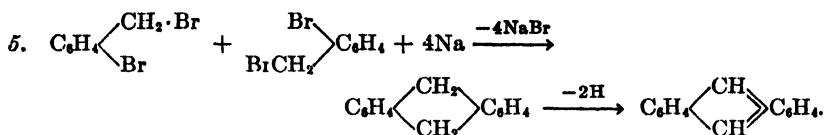
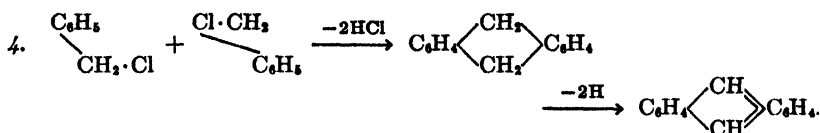
Anthracene (from the Greek *ανθραξ*, coal), which, together, with its isomer, phenanthrene, occurs in the highest boiling fraction of coal-tar, is the parent substance of a large group of substances, to which belong the important dyes of the madder root, alizarin, purpurin, etc., and a series of other vegetable products.

*Synthetic methods of formation of anthracene derivatives.*—1. From benzene, acetylene tetrabromide and aluminium chloride, anthracene itself is obtained (*Anschütz*, Ber. 16, 623). 2. Anthracene is also obtained from chloroform, benzene, and aluminium chloride (*Kolliker*, Ann. 228, 255) and from methylene bromide, benzene, and aluminium chloride, hydrogen being split off from the dihydroanthracene first formed. 3. Anthracene is obtained from benzene and ethylene by passing the vapours through a tube heated to 800–1000° (*Zanetti*, Ind. Eng. Chem. 13, 208). 4. Dihydroanthracene, and therefore anthracene, is formed from 2 mols. of benzyl chloride with aluminium chloride, toluene being a by-product (*Perkin, Jr.*, J. 37, 726), or from benzyl chloride and water at 200° (*Limpricht*, Ann. 139, 308), di-benzyl (p. 558) being a by-product.

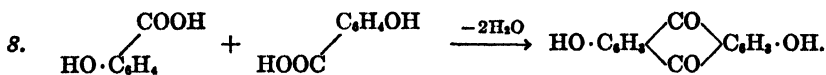
Anthracene is also formed by the action of aluminium chloride on diphenylmethane. It is probable that decomposition of diphenylmethane into benzyl chloride and benzene first occurs. In a similar way *as*-diphenylethane (p. 552) gives *ms*-dimethylantracene (*Tassinari*, Ber. 27, 3238).

5. *o*-Bromotoluene readily splits off HBr and gives anthracene when superheated (*Meyer*, Mo. 38, 141). Dihydroanthracene is obtained from 2 mols. *o*-bromobenzyl bromide by the action of sodium (*Loring-Jackson*, Ber. 12, 1965) (see p. 668):



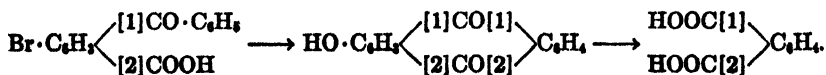


6a. Anthraquinone is formed from phthalyl chloride and benzene, by the action of zinc dust. 6b. Similarly, when phthalic anhydride is heated with 1 mol. of a mono- or polyhydric phenol and sulphuric acid at 150°, hydroxyanthraquinones are formed, and if an excess of phenol is present, phthaleins are obtained (cf. p. 545). 7. When *o*-benzoylbenzoic acid is heated with phosphorus pentoxide or conc. sulphuric acid, anthraquinone is formed. Substituted benzoylbenzoic acids give substituted anthraquinones. In a similar way benzylbenzoic acid gives anthrone (p. 651). 8. Di- and tetrahydroxyanthraquinones are formed when *m*-hydroxy- and *m,m'*-dihydroxybenzoic acids are heated with sulphuric acid:

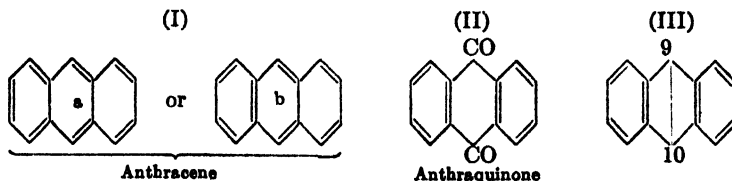


This series of methods of preparation, and others, such as the formation of anthraquinone from *o*-tolyl-phenyl-ketone and lead oxide, anthracene and methyl anthracene from *o*-tolyl-phenyl-ketone and *o*-ditolyl-ketone and zinc dust (*Elbs*, J. pr. [2], 41, 1, 121), confirm the symmetry of anthracene derivatives, which is also indicated by the following facts:

Brominated *o*-benzoylbenzoic acid from phthalic acid (p. 523) gives bromo-anthraquinone; the hydroxyanthraquinone obtained from this can be oxidised to phthalic acid. Phthalic acid is thus used in making the molecule, and is also obtained by its decomposition, this being connected in the first case with one half of the molecule, and in the second with the other (cf. constitution of naphthalene, p. 610) (*Pechmann*, Ber. 12, 2124):

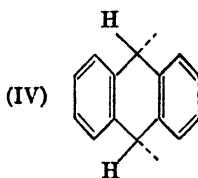


Anthraquinone, and anthracene, which is genetically connected with it, must therefore have formulae corresponding to I and II:



On the basis of the above methods of formation, a third formula for anthracene, with a bridge between the 9 and 10 carbon atoms (III) was formerly put forward. Against this, the oldest formula of *Graebe* and *Liebermann*, there are a series of important facts: 1. It is possible to synthesise anthracene from a naphthalene derivative. *Colver* and *Noyes* condensed the ester of  $\Delta^2$ -dihydronaphthoic acid with acetoacetic ester. After hydrolysis of the product, 2,4-diketo-octahydroanthracene was obtained, carbon dioxide being split off, and this gave anthracene on distillation with zinc dust (Am. 43, 898). 2. Anthracene reacts with maleic anhydride as a typical diene, and takes up one molecule in the middle ring to give a condensation product (*Diels*, Ann. 486, 191). 3. Sodium readily adds on to anthracene. This fact is best explained by the *Armstrong-Hinsberg* formula (Ia), since this contains conjugated double bonds in the middle ring. 4. The spectrochemical behaviour of anthracene agrees with an "ortho-quinoid" configuration (*Hinsberg*, Ann. 319, 284; 486, 191; *Schlenk*, Ber. 47, 479; *Auwers*, Ber. 53, 941). 5. A model, built up from the known radii of the atoms, shows that the 9 and 10 carbon atoms are separated by far too great a distance to be bridged by the usual C—C link (*Meyer*, Z. angew. Ch. 41, 937).

The positions 1,4,5,8( $\alpha$ -) and 2,3,6,7( $\beta$ -) in anthracene are equivalent. Replacement of the two middle hydrogen atoms gives rise to 9- and 10-,  $\gamma$ -, or meso-derivatives. In contrast to this, substituents in the two other benzene nuclei are called benz-. In most reactions of anthracene it is the middle carbon atoms that are first attacked. This reactivity has been explained by *Clar* by supposing that a more or less large number of molecules of a di-radical (IV) are present in equilibrium with (I) (Ber. 64, 2194):



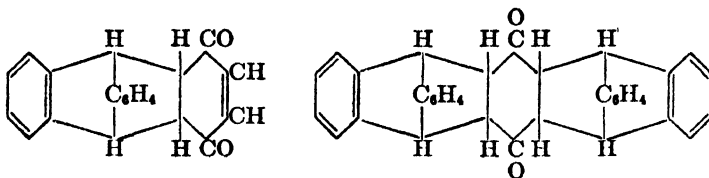
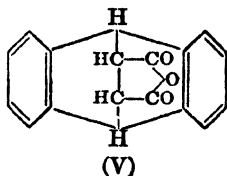
**Anthracene**,  $C_{14}H_{10}$ , m.p.  $218^\circ$ , b.p.  $340^\circ$ , is isomeric with phenanthrene (p. 668), and is obtained by the methods outlined on pp. 645, 646 (see also *Delacre*, C.r. 120, 155). It is found in large quantities in coal-tar.

Commercial crude anthracene, which boils at  $340$ – $360^\circ$ , can be purified by treatment with liquid sulphur dioxide, which dissolves out most of the impurities (Ger. Pat. 68,474). For other methods of purification, see *Schulze*, Ber. 18, 3034; Ger. Pat. 42,053; *Zeidler*, Ann. 191, 288; Ger. Pat. 122,852). Chemically pure anthracene is obtained by heating anthraquinone with zinc dust.

Anthracene crystallises in colourless, monoclinic tablets with a beautiful blue fluorescence. It is difficultly soluble in alcohol and ether, but dissolves readily in hot benzene. It forms the molecular compound  $C_{14}H_{10} \cdot C_6H_5(NO_2)_3OH$ , with picric acid, red needles, m.p.  $138^\circ$ .



If a saturated solution of anthracene in benzene, or better in xylene (*Lineberger*, Am. Ch. J. 14, 597) is exposed to sunlight, a dimolecular modification, known as **paranthracene**, ( $C_{14}H_{10}$ )<sub>2</sub>, separates. It melts at 270–280°, with formation of ordinary anthracene. It is difficultly soluble in benzene, and is not attacked by bromine or nitric acid (*Luther*, Z. physikal. Chem. 53, 385). By means of X-ray photographs it has been shown that the linkage between the two anthracene nuclei takes place in the meso-position. The formation of paranthracene can be explained as a polymerisation of the di-radical (IV) (*Hengstenberg*, An. soc. espan. fisica quim. 30, 5). Anthracene forms an addition product with maleic anhydride (V), m.p. 262–263°, which breaks down to a *cis*-dicarboxylic acid, m.p. 251–253°, with alkali. On heating, the addition product breaks down again into its components. Similar compounds have been obtained with crotonic and citraconic anhydrides (*Diels*, Ann. 486, 191). With quinone, addition products of the following type are formed (*Clar*, Ber. 64, 1676):



**ALKYLATED ANTHRACENES:** (a)  $C_6H_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} C_6H_4R$ , benz-alkyl deriva-

tives; (b)  $C_6H_4 \begin{smallmatrix} \text{CR} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} C_6H_4$ , *ms*- or  $\gamma$ -alkyl derivatives. (a) The benz-mono-alkyl-anthracenes can exist in two isomers ( $\alpha$ - and  $\beta$ -).

1-( $\alpha$ -)Methylantracene,  $C_6H_4(CH_3)C_6H_4[1]CH_3$ , m.p. 86°, has been obtained by distilling 1,4-chloromethylantraquinone with zinc dust (*Fischer*, J. pr. [2], 83, 201).

2-( $\beta$ -)Methylantracene,  $C_6H_4(CH_2)C_6H_4[2]CH_3$ , m.p. 207°, is very similar to anthracene itself, and is found in the crude anthracene from coal-tar. It is formed by pyrolysis of ditolylmethane and ditolylethane (*Fischer*, J. pr. [2], 79, 555), and by boiling benzoyl-xylene,  $C_6H_5CO \cdot C_6H_4(CH_3)_2$ , by reduction of 2-methylantraquinone with zinc dust (*Limpricht*, Ann. 311, 181), and from the vegetable substances chrysophanic acid, emodin, and dermocybenes, which are hydroxylated methylantraquinones (p. 665). When oxidised with nitric acid, methylantracene gives methylantraquinone, and with chromic acid mixture there is simultaneous oxidation of the methyl group giving anthraquinone carboxylic acid (p. 666). It polymerises in sunlight to dimethyl-dianthracene, m.p. 229°, in the same way as anthracene itself (*Orndorff*, Am. Chem. J. 22, 152).

1,6- and 2,6-Dimethylantracene,  $C_{14}H_{12}(CH_3)_2$ , m.p. 240° and 244°, are produced together from toluene and methylene chloride or acetylene tetrabromide in the presence of aluminium chloride, by the second method of formation given above. The 2,6-compound is also obtained by boiling *m*-xylyltolyl ketone (*Lavauz*, Ann. chim. phys. [8], 20, 433; 21, 131; *Seer*, Mo. 32, 143). A dimethylantracene is obtained from the high boiling aniline oils of coal-tar.

2,7-Dimethylantracene, m.p. 243.5°, is obtained, together with a little 1,6-dimethylantracene from the condensation of toluene and acetylene by means of aluminium chloride (*Cook*, Am. 43, 334). It can also be obtained by removal of water from 2,4,4'-trimethylbenzophenone. In a similar way 2,6-dimethyl-

anthracene (*Morgan*, J. 1929, 2203), 1,3-dimethylantracene (*von Braun*, Ber. 59, 914), and 2,3,6-trimethylantracene (*Morgan*, J. 1929, 2551) are obtained from 2,5,4'-trimethylbenzophenone. For 1- and 2-phenylantracenes, m.p. 110–112° and m.p. 207°, respectively, see *Cook*, J. 1930, 1087.

2,3,6,7-Tetramethylantracene, m.p. 301°, is found in the tar from bituminous coal submitted to low temperature carbonisation, and has also been synthesised (*Morgan*, J. 1931, 2323).

(b) *Meso*- or  $\gamma$ -alkylantracenes are obtained from the alkylated hydranthranols,

$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CR(OH)} \diagdown \\ \diagdown \text{CH}_2 \diagup \end{array} \text{C}_6\text{H}_4$  (p. 655), by removal of water by boiling with alcohol,

hydrochloric acid, or picric acid (*Liebermann*, Ann. 212, 100), and by the action of alkyl magnesium salts on anthrone (p. 651) (*Krollpfeiffer*, Ber. 56, 1617). On oxidation they give alkyl-oxanthrones (p. 653).  $\gamma$ - or 9-Methylantracene, m.p. 79–80°; 9-ethyl-, isobutyl-, amyl-antracenes melt at 60°, 57°, 61°.

$\gamma$ - or 9-Phenylantracene,  $\text{C}_{14}\text{H}_{12}\text{C}_6\text{H}_5$ , m.p. 152°, is obtained by reduction of phenylantrone (p. 653).  $\gamma, \gamma$ - or 9,10-Diphenylantracene,  $\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2$ , m.p. 240°, is obtained by the reduction of diphenyldihydroxydihydro-antracene with zinc dust and glacial acetic acid (*Heller*, C.r. 138, 1251; *Guyot*, Bull. [3], 33, 1104).

$\gamma, \gamma$ - or 9,10-Dimethylantracene,  $\text{C}_6\text{H}_4(\text{C}_6\text{H}_3)_2$ , m.p. 179°, is obtained from its dihydro-compound, the condensation product of ethylidene chloride and benzene with aluminium chloride (p. 655) (*cf. Anschütz*, Ann. 235, 305). 9,10-Dibenzyl-antracene,  $\text{C}_6\text{H}_4(\text{C}_6\text{H}_5\text{CH}_2)_2$ , m.p. 240°, is obtained by prolonged boiling of anthracene with benzyl chloride and a little zinc dust in carbon disulphide solution (*Lippmann*, Mo. 23, 672; 25, 793). For the di-radical nature of 9,10-diphenyl-antracene, see Vol. IV.

The 9,10-dialkyl-antracenes are solids, while their dihydro-compounds are liquids. The former readily add on sodium, and then react with alkyl halides giving tetra-alkyl compounds (*Hugel*, Bull. [4], 53, 1498).

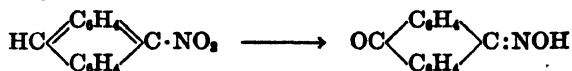
**SUBSTITUTED ANTHRACENES.** When halogens act on anthracene, addition products are first formed, in which the halogen is loosely bound. When these are heated, or treated with alkalis, substitution products result. By the action of chlorine on anthracene in benzene, dichloroanthracene tetrachloride, m.p. 205–207° is formed; it can easily be reduced to 9,10-dichloroanthracene, m.p. 209–210°. Anthraquinone chloride, m.p. 170°, is formed as a by-product. By heating, or treatment with alcoholic potash, dichloroanthracene tetrachloride gives two isomeric tetrachloro-anthracenes. The action of bromine on anthracene gives similar compounds. Two dibromoanthracene tetrabromides are known,  $\alpha$ - m.p. 134–135°, and  $\beta$ - m.p. 180–182°. The  $\beta$ -form is obtained by the action of bromine vapour on anthracene. The  $\alpha$ -form is obtained by the action of bromine on anthracene in chloroform. The  $\alpha$ -compound when dissolved in benzene, rapidly gives up 4 bromine atoms on exposure to sunlight, and goes into 9,10-dibromoanthracene. The  $\beta$ -compound remains unchanged under these conditions (*Meyer*, A. 396, 166). For other chloro-, bromo-, and chloro-bromo-anthracenes, see *Liebermann*, Ber. 47, 1011; *Barnett, et al.*, J. 125, 1084; Rec. 43, 530; 44, 894; 45, 68, 558.

Nitric acid readily gives anthraquinone and nitrated anthraquinones with anthracene. If, however, nitration is carried out in acetic acid solution with a mixture of nitric acid and acetic anhydride at 15–20°, 9-nitroanthracene,  $\text{C}_{14}\text{H}_9\text{NO}_2$ , yellow needles, m.p. 145–146°, which can be distilled under reduced pressure, and 9,10-dinitroanthracene,  $\text{C}_{14}\text{H}_8(\text{NO}_2)_2$ , m.p. 294°, are formed. When an alcoholic solution of 9-nitroanthracene is exposed to sunlight, it breaks down into anthraquinone and nitrous acid, acetaldehyde being also formed (*Baileguy*, Bull. [4], 31, 915). The nitro-compounds are more easily obtained by indirect methods. If anthracene is digested in acetic acid with 1 mol. of nitric acid at 30–35°, the acetate of nitrohydranthranol,

$\text{CH}_3\text{COO} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C} \begin{array}{c} \diagup \text{NO}_2 \diagdown \\ \diagdown \text{H} \diagup \end{array}$ , is formed. With

HCl this gives the corresponding chloride, with nitrogen trioxide, the nitrite, and with alcohol, the ether, which can also be obtained directly by nitrating the alcohol with nitric acid. When the chloride is treated with caustic soda it gives 9-nitroanthracene. If this is treated with nitrogen dioxide in chloroform, 9,9,10-

trinitro-9,10-dihydro-anthracene,  $(\text{NO}_2)_2\text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{CH}(\text{NO}_2)$ , is formed, which gives 9,10-dinitroanthracene with caustic soda. In a similar way, 9-ethyl-10-nitroanthracene,  $\text{C}_{14}\text{H}_8(\text{C}_2\text{H}_5)(\text{NO}_2)$ , m.p.  $135^\circ$ , is obtained from ethyl-anthracene. When 9-nitroanthracene is heated with alcoholic potash, anthraquinone-oxime is formed, *via* an intermediate product, which is produced by the addition of potassium ethylate:



(*cf.* 9-nitrophenanthrene, p. 672). If anthracene is acted upon by nitric acid in isobutyl alcohol, nitro-anthrone,  $\text{CO}(\text{C}_6\text{H}_4)_2\text{CH} \cdot \text{NO}_2$ , is formed (*cf.* anthrone, p. 651) (*Meisenheimer*, Ann. 330, 133; *Hantzsch*, Ber. 42, 1216).

9- or Meso-aminoanthracene, or *anthramine*, m.p.  $143\text{--}150^\circ$ , is obtained by reducing 9-nitro-anthracene with stannous chloride and hydrochloric acid. 9-Anthramine, like 1-( $\alpha$ )-anthramine, m.p.  $119^\circ$ , and 2-( $\beta$ )-anthramine, m.p.  $237^\circ$ , is also obtained from the corresponding hydroxy-anthracenes by heating with ammonia (*Dienel*, Ber. 38, 2862). 9-Aminoanthracene combines with phenyl diazonium chloride to give benzene-azo-meso-anthramine,  $\text{C}_6\text{H}_5\text{N} : \text{N} \cdot \text{C}_{14}\text{H}_8 \cdot \text{NH}_2$ , m.p.  $183^\circ$ , which is decomposed by acids into anthraquinone, phenylhydrazine, and ammonia (*Kauffer*, Ber. 40, 518), and is reduced to the readily oxidisable 1,4-anthradiamine (*Pisorschi*, Ber. 41, 1434). Dinitroanthracene cannot be reduced to diamino-anthracene. Meso-phenylanthramine, m.p.  $203^\circ$ , see *Padova*, C.r. 149, 217.

Anthracene sulphonic acids are formed by the action of sulphuric acid on anthracene, and by the reduction of anthraquinone sulphonc acids (p. 660). In acid medium, equivalent quantities of 1- and 2-sulphonic acid are formed, and are best separated by means of their barium salts. 1-Anthracene sulphonic acid, see *Schmidt*, Ber. 37, 70. By careful treatment of anthracene with dilute sulphuric acid, 2-anthracene monosulphonic acid,  $\text{C}_{14}\text{H}_9 \cdot \text{SO}_3\text{H}$ , is formed. Its chloride melts at  $122^\circ$  (*Hefter*, Ber. 28, 2258). By the action of conc. sulphuric acid, 1,5- and 1,8-anthracene disulphonic acids are formed (chlorides m.p.  $249^\circ$ ,  $225^\circ$ , respectively). 9-Anthracene sulphonic acid is obtained by the action of sodium sulphite on 9-nitroanthracene. The sulphonic acid group is readily split off by boiling with acids, and anthracene is reformed (*Minajew*, J. Russ. Phys.-Chem. Soc. 61, 143).

**Hydroxyanthracenes:** 1.  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CH} \diagdown \\ \diagdown \text{CH} \diagup \end{array} \text{C}_6\text{H}_4\text{OH}$ ; 2.  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{COH} \diagdown \\ \diagdown \text{CH} \diagup \end{array} \text{C}_6\text{H}_4$ . (1)

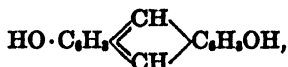
1- and 2-Monohydroxyanthracenes,  $\alpha$ - and  $\beta$ -anthrols, resemble the phenols of naphthols. 1-Anthrol is obtained by fusing 1-anthracene monosulphonic acid with potash, and forms yellowish leaflets, m.p.  $152^\circ$  (*Schmidt*, Ber. 37, 71).  $\beta$ -Anthrol decomposes at  $200^\circ$ , and is obtained from 2-anthracene sulphonic acid and from 2-hydroxy-anthraquinone. 1-Anthrol reacts with nitrous acid forming 2- and 4-nitroso-1-anthrol,  $\text{C}_6\text{H}_4(\text{CH})_2\text{C}_6\text{H}_2(\text{OH})(\text{NO})$ , while 2-anthrol gives the isomeric 1-nitroso-2-anthrol. When reduced, these nitroso-anthrols give 2- and 4-amino-1-anthrol, and 1-amino-2-anthrol. When oxidised with ferric chloride

the nitroso-anthrols give 1,2-anthraquinone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} - \text{C} - \text{CO} - \text{CO} \\ \diagdown \quad \diagup \\ \text{CH} - \text{C} - \text{CH} = \text{CH} \end{array}$ , m.p.

$180^\circ$  (decomp.), and 1,4-anthraquinone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} - \text{C} - \text{CO} - \text{CH} \\ \diagdown \quad \diagup \\ \text{CH} - \text{C} - \text{CO} - \text{CH} \end{array}$ , m.p.  $208^\circ$

(decomp.), isomeric with ordinary anthraquinone. In their properties and reactions, these resemble in all respects 1,2- and 1,4-naphthaquinone (*Dienel*, Ber. 39, 926; *Pisorschi*, Ber. 41, 1434; *Lagodzinski*, Ann. 344, 78). 1,2-Anthrahydroquinone,  $\text{C}_6\text{H}_4(\text{CH})_2\text{C}_6\text{H}_2(\text{OH})_2$ , m.p.  $131^\circ$  (decomp.), is formed when 1,2-anthraquinone is reduced with zinc dust and glacial acetic acid (*Lagodzinski*, Ann. 342, 59). The anthrols can be oxidised to hydroxyanthraquinones by means of chromic acid if the OH group is first acetylated (*cf.* oxidation of phenols, p. 188). 1,2-Anthrahydroquinone gives alizarin (p. 662) when treated in this manner.

**Benz-dihydroxyanthracenes:** 1,8- and 1,5-dihydroxyanthracene,



**chrysazol** and **rufol**, m.p. 225° and 265°, are obtained from 1,8- and 1,5-anthracene disulphonic acids (*Lampe*, Ber. 42, 1413), and give the corresponding dihydroxyanthraquinones, **chrysazin** and **anthrarufin** (p. 664) on oxidation and hydrolysis of their acetyl derivatives. **2,3-Dihydroxyanthracene**, decomposing at 180°, is obtained by reduction of dimethoxyhystazarin with zinc dust and ammonia, and hydrolysis with hydriodic acid (*Lagodzinski*, Ann. 342, 90). Other hydroxyanthracenes have been obtained by the reduction of the corresponding hydroxyanthraquinones with aluminium amalgam and ammonia (*Hall*, J. 123, 2029).

(2) 9-( $\gamma$ - or *ms*-)**Hydroxyanthracene**, **anthranol**,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C(OH)} \\ \diagdown \text{CH} \end{array} \text{C}_6\text{H}_4$ , forms brownish-yellow needles, and is unstable. It melts, when rapidly heated at 120°, and is desmotropic with **anthrone**,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CH}_2 \end{array} \text{C}_6\text{H}_4$ . The latter exists in colourless, lustrous needles, m.p. 155°, and is stable (*Meyer*, Ann. 379, 37). **Anthrone** is obtained synthetically from *o*-benzyl-benzoic acid,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CH}_2\text{C}_6\text{H}_5 \\ \diagdown \text{COOH} \end{array}$

(p. 522), by the action of conc. sulphuric acid at 90°, and from phthalide chloride (p. 376), benzene, and aluminium chloride. It can also be obtained by the reduction of anthraquinone with zinc, or zinc and acetic acid, when it is accompanied by dianthryl,  $(\text{C}_{14}\text{H}_9)_2$  (*Meyer*, Ann. 379, 55; Ger. Pat. 201,542). **Anthranol acetate**, m.p. 134°, is also formed by the oxidation of anthracene with lead dioxide in glacial acetic acid (*Meyer*, Ann. 379, 75). **Anthrone** is insoluble in cold alkalis, but it dissolves on warming, forming salts of anthranol, which can be obtained from the solutions of the salts by careful addition of sulphuric acid. The isomers which can exist in the solid state, are in equilibrium in solution or in the melt, in which the more stable anthrone strongly predominates. The solutions therefore show the properties of both forms. On heating with acetic anhydride, anthranol acetate is formed, and methylation with dimethyl sulphate leads to the formation of the methyl ether without nuclear substitution. **Anthranol methyl ether** melts at 94°. On the other hand, alkylation with ethyl iodide and caustic potash leads

to the formation of a mixture of **anthranol ethyl ether**,  $\text{HC} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{COC}_2\text{H}_5$ ,

**ethyl-anthranol ethyl ether**,  $\text{C}_2\text{H}_5 \cdot \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{COC}_2\text{H}_5$ , m.p. 77°, and **diethyl-**

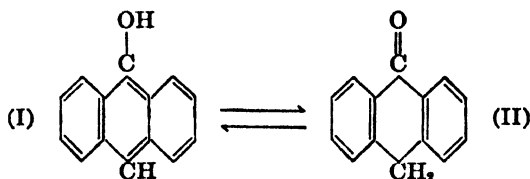
**anthrone**,  $(\text{C}_2\text{H}_5)_2\text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{CO}$ , m.p. 136° (*Goldmann*, Ber. 21, 2505). **Anthrone** condenses with benzaldehyde in the presence of pyridine forming **benzylidene anthrone**,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{C}_6\text{H}_4)_2\text{CO}$ , yellow needles, m.p. 127° (*Haller*, C.r. 141, 857). It condenses with benzophenone chloride to give **diphenylanthra-**

**quinomethane**,  $\text{C}_6\text{H}_5\text{N}=\text{N}-\text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{C} \cdot \text{OH}$ , m.p. 196° (*Padova*, Ann. chim. phys. [8], 19, 353). With phenyldiazonium chloride it gives **benzene-azo-**

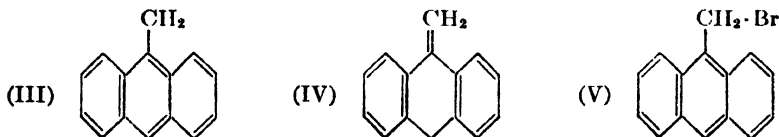
**anthranol**,  $\text{C}_6\text{H}_5\text{N}=\text{N}-\text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{C} \cdot \text{OH}$ , m.p. 183°, which can also be obtained

by the action of phenylhydrazine on dibromo-anthrone,  $\text{Br}_2\text{C}(\text{C}_6\text{H}_4)_2\text{CO}$ , m.p. 157°. **Anthraquinone-monophenylhydrazone**, which might be expected, appears to be unstable (*Kaufler*, Ber. 40, 518; *Meyer*, Ann. 396, 152).

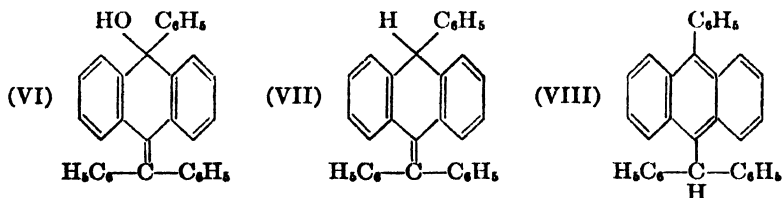
**TRANS-ANELLAR TAUTOMERISM.** The tautomerism between anthranol (I) and anthrone (II), is brought about by the migration of a hydrogen atom "across the ring." This phenomenon has been called "trans-anellar tautomerism" by *Barnett*.



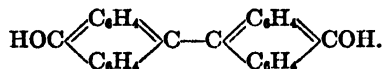
A similar tautomerism is found in the *ms*-alkyl-anthracenes. Thus the action of bromine on 9-methyl-anthracene (III) gives  $\omega$ -bromomethyl-anthracene (V), which is actually produced from the tautomeric form (IV):



For the more complicated *ms*-alkyl-anthracenes there are true isomers. Thus 9-benzhydrylidene-10-phenyl-10-hydroxy-9,10-dihydro-anthracene (VI) gives 9-benzhydrylidene-10-phenyl-9,10-dihydro-anthracene (VII) and 9-benzhydryl-10-phenyl-anthracene (VIII) on reduction (*Barnett*, *Ber.* 59, 767; 62, 3063; *Bergmann*, *Ber.* 63, 1037):



Anthrone and anthranol are oxidised by atmospheric oxygen, or by gentle oxidising agents such as ferric chloride, mercuric oxide, *etc.*, to meso-dihydrodianthrone,  $\text{CO}(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{CH}(\text{C}_6\text{H}_5)_2\text{CO}$ , m.p.  $245^\circ$ . This substance can also be obtained from monobromoanthrone, m.p.  $148^\circ$ , by heating with copper powder. It is insoluble in alkalis, but dissolves in warm alcoholic alkali to give the alkali salt of dianthranol,



Dianthranol forms yellow crystals, m.p.  $230^\circ$ . It is easily obtained by the reduction of anthraquinone with zinc dust and caustic soda under pressure at  $160^\circ$ , and isomerises to meso-dihydrodianthrone in the presence of alcoholic hydrochloric acid. When oxidised with ferric chloride or copper sulphate it is converted into meso-dianthrone,  $\text{CO}(\text{C}_6\text{H}_5)_2\text{C}:\text{C}(\text{C}_6\text{H}_5)_2\text{CO}$ , a lemon yellow powder, a dinuclear quinone with a constitution similar to that of diphenoquinone (p. 503). It gives dianthranol again when treated with zinc dust and acetic acid (*Meyer*, *Mo.* 30, 165). 2-Methyl-anthrone, m.p.  $87^\circ$  (*Padona*, *Ann. chim. phys.* [8], 19, 353).

2-Hydroxy-anthrone,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix}\rangle\text{C}_6\text{H}_4(\text{OH})$ , m.p.  $221^\circ$ , is prepared from

hydroxydiphenylmethane-*o*-carboxylic acid. **Dimethylamino-anthrone**,  $C_{14}H_{10}O$ -[N(CH<sub>3</sub>)<sub>2</sub>], m.p. 80–85°, has been obtained by the action of sulphuric acid on *o*-dimethylamino-benzyl-benzoic acid (Limpricht, Ann. 307, 313).

**1-Hydroxyanthrone**, m.p. 135°, exists in equilibrium with 1-hydroxy-anthranol. The hydroxyl-group in the 1-position favours the keto-form, but in the 10-position it exerts an opposite effect, since anthrahydroquinone is stable but hydroxyanthrone is not. For the equilibrium of polyhydric anthrones and anthranols, see Meyer, Ann. 420, 113.

**A dihydroxyanthrone**,  $C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown CH_2 \end{array} C_6H_2(OH)_2$ , so-called **anthrarobin**, has been obtained by the reduction of alizarin with zinc dust and ammonia. It is used as a remedy for skin diseases. Some isomeric dihydroxy-anthrols have been obtained by the reduction of quinazarin, anthrarufin, hystazarin, and chrysazin (p. 664) with hydriodic acid (Pleus, Ber. 35, 2923, 2930; Schrobsdorff, Ber. 36, 2938).

For polyhydroxy-anthranols, see Cross, J. 1930, 292; Zahn, Ber. 67, 2063.

**ms-Phenylanthrone**,  $C_6H_5CH(C_6H_4)_2CO$ , m.p. 141–144°, is obtained by the action of sulphuric acid on triphenylmethane-*o*-carboxylic acid (see p. 543), or from bromoanthrone, benzene, and aluminium chloride (Barnett, J. 123, 2631). When oxidised it gives phenyloxanthrone, and on reduction, phenylanthracene. **ms-Phenylanthranol** is obtained by dissolving *ms*-phenylanthrone in hot alkali and precipitating with acids. It readily isomerises to the original substance. Substituted phenylanthrones are obtained from substituted triphenylmethane-carboxylic acids (Guyot, Bull. [3], 17, 966). According to their origin, the hydroxylated phenylanthrones, such as **dihydroxyphenylanthrone**,

$HOC_6H_4CH \begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_3(OH) \end{array} CO$ , should be regarded as phthalidines, since they are produced from the phthalins, the reduction products of the phthaleins or diphenolphthalides (p. 546). The phthalidines give phthalideins, or dihydroxyphenyloxanthrones, on oxidation.

**Diphenylanthrone**,  $C_6H_5 \begin{array}{c} \diagup C(C_6H_5)_2 \\ \diagdown CO \end{array} C_6H_4$ , m.p. 192°, is a derivative of anthrone. It is obtained from *as*-phthalylene tetrachloride (p. 385) by condensation with benzene, and from phenyloxanthrone by the action of benzene and sulphuric acid (Haller, C.r. 121, 102). When reduced with zinc dust and glacial acetic acid it gives 9,9-diphenyl-dihydroanthracene (p. 655). Mixed diarylanthrones are obtained either from phenyloxanthrone, benzene homologues and sulphuric acid, or from benzene derivatives and aluminium chloride and **phenyloxanthranyl chloride**,  $CO \begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} C \begin{array}{c} \diagup C_6H_5 \\ \diagdown Cl \end{array}$ , m.p. 164°. This compound is prepared from diphenylphthalide (p. 544), by heating with phosphorus pentachloride to 140° (Guyot, Bull. [3], 17, 966; Tétray, C.r. 128, 1406). It condenses with phenols on merely warming, giving hydroxydiphenyl-anthrones (Liebermann, Ber. 38, 3802). **ms-Dichloroanthrone**,  $CO(C_6H_4)_2CCl_2$ , m.p. 133°, is obtained from *o*-tolyl-phenyl ketone by heating with chlorine to 120°, and by the action of chlorine on anthrone. With dimethylaniline and aluminium chloride it gives **tetramethyl-diamino-diphenylanthrone**,  $[(CH_3)_2NC_6H_4]_2C(C_6H_4)_2CO$ , in yellow needles, m.p. 278° (Haller, C.r. 136, 535).

For other chloroanthrones, see Barnett, J. 123, 2549. For *p*-anilido- and *p*-nitro-anthrone, m.p. 154–156°, and m.p. 137°, respectively, see Meyer, Ann. 396 145. For other benzyl- and amino-derivatives of anthrone, see Julian, Am. 56, 2174; Jones, J. 1934, 1813.

The group of anthracoumarins can also be derived from anthrone. They are obtained by condensation of cinnamic acid and hydroxybenzoic acids with sulphuric acid. **Anthracoumarin**,  $\begin{array}{c} C_6H_4-C=CH \\ | \quad \quad | \\ CO-C_6H_3-O \end{array} CO$ , m.p. 260°, is obtained from *m*-hydroxybenzoic acid and cinnamic acid. **Dihydroxyanthracoumarin**, or styrogallol, is obtained from gallic acid and cinnamic acid (Jacobsen, Ber. 20, 2588;

*Kostanecki*, Ber. 20, 3143; *Slama*, Dissertation, Giessen, 1899, 29; C. 1899, II, 967).

*ms*-Dihydroxyanthracene, anthrahydroquinone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{C(OH)} \end{array} \text{C}_6\text{H}_4$ , forms brown needles. The diacetyl-compound melts at  $260^\circ$ . It is desmotropic with oxanthrone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH(OH)} \end{array} \text{C}_6\text{H}_4$ , which forms yellowish-white needles, m.p.

$167^\circ$ . The two compounds bear the same relationship to each other as anthranol and anthrone (pp. 651, 657), but the conversion of one into the other in solution is exceedingly slow. In this case it is the enol form, anthrahydroquinone, that is the more stable. Anthrahydroquinone is formed by the reduction of anthraquinone with zinc dust and caustic potash, and soon reoxidises in the air to anthraquinone. It readily dissolves in alkalis giving a red solution. By treatment with alcoholic hydrochloric acid it is partially converted into oxanthrone. Oxanthrone itself is easily obtained by heating bromanthrone with aqueous acetone or, directly, by the action of bromine on anthracene in an aqueous acetone solution. When reduced with zinc dust and glacial acetic acid, anthranol and anthrone are formed. On heating with alkali, or alcoholic hydrochloric acid, oxanthrone isomerises to anthrahydroquinone. When anthrahydroquinone is alkylated with alkyl iodides or dialkyl sulphates and alkali, the mono- and di-alkyl ethers of

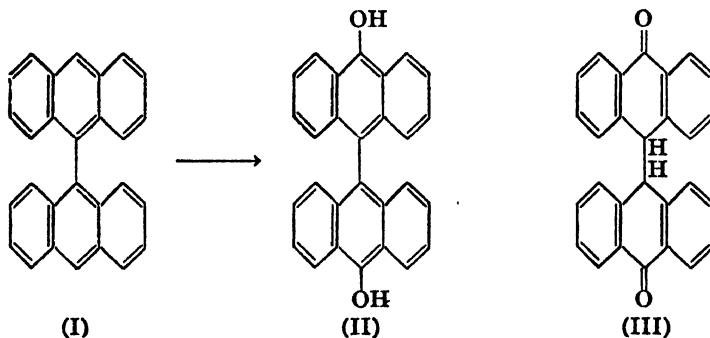
anthrahydroquinone and alkyloxanthrone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C(OH)Alk} \end{array} \text{C}_6\text{H}_4$ , are obtained together (*Meyer*, Ann. 379, 43).

**ANTHRACENE CARBOXYLIC ACIDS:** 1- and 2-Anthracene carboxylic acids,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{array} \text{C}_6\text{H}_2 \cdot \text{COOH}$ , m.p.  $245^\circ$  and  $281^\circ$ , are obtained from their

nitriles, which are themselves prepared from the anthracene sulphonic acids by the action of potassium cyanide. The 2-acid is also obtained by the reduction of anthraquinone-2-carboxylic acid (p. 666). *ms*-Anthracene carboxylic acid, m.p.  $217^\circ$  (decomp.), is obtained from its chloride, which is itself prepared from anthracene and carbonyl chloride, or better oxalyl chloride at  $160^\circ$  (*Liebermann*, Ber. 44, 205), or from anthracene, cyanogen bromide, and aluminium chloride (*Karrer*, Helv. 2, 482). 1-, 2-, and 9-Anthracene carboxylic acids polymerise when exposed to light, but depolymerise again in the dark (*Weigert*, Ber. 47, 898). 1,5- and 1,9-Anthracene dicarboxylic acids are also known (*Kardos*, Ber. 46, 2086; *Coulson*, J. 1930, 1931).

*ms*-Benzoyl-anthracene, anthraphenone,  $\text{C}_{14}\text{H}_9 \cdot \text{COC}_6\text{H}_5$ , m.p.  $148^\circ$ , is obtained from anthracene, benzoyl chloride, and zinc dust or aluminium chloride. In the latter case, two isomers, m.p.  $75^\circ$  and  $203^\circ$ , are also obtained (*Perrier*, Ber. 33, 816; *Lippmann*, Ber. 34, 2766).

Dianthryl (I) (= dianthranyl), a white substance, m.p.  $300^\circ$ , is obtained by the reduction of anthraquinone with tin or zinc and hydrochloric acid (Ber. 20, 1855). By oxidising acetylation it can be converted into dianthranol acetate



(Eckert, Mo. 36, 497; Barnett, J. 123, 380). Dianthranol (II), m.p. about 230°, can also be regarded as an enol form of dianthrone (III). It is obtained from the keto form (III) by treatment with alcoholic potash. It is formed from anthraquinone by treatment with zinc powder and 10% caustic soda (Meyer, Ber. 42, 144). Dianthranol gives dianthrone (III) when heated with alcoholic hydrochloric acid. This compound melts about 250° with decomposition (Meyer, Mo. 30, 173). Dianthrone is formed when anthracene is oxidised with nitric acid in glacial acetic acid, or from bromoanthrone with bases such as piperidine, methylamine, etc. (Barnett, J. 121, 2059; 123, 380). Hydroxy-dianthrils and hydroxy-dianthrone are also known (Perkin, J. 121, 289; Haller, J. 125, 231; Goodall, J. 125, 470). A 2,2'-dianthrill, m.p. 355°, is formed by distilling tetrahydroxy-2,2'-dianthraquinoyl with zinc dust (Scholl, Ber. 52, 1829).

**HYDROANTHRACENES.** Dihydroanthracene,  $C_{14}H_{12}$ , m.p. 108°, is formed by the reduction of anthracene with sodium amalgam and alcohol. It has also been obtained synthetically by various methods (p. 645). The two additional hydrogen atoms are in the 9,10-position. Reduction of anthracene with hydriodic acid or with hydrogen and nickel at 200–250° gives anthracene-tetra-, -hexa-, -octa-, and perhydrides,  $C_{14}H_{14}$ ,  $C_{14}H_{16}$ ,  $C_{14}H_{18}$ , and  $C_{14}H_{24}$ , m.p. 89°, 63°, 73–74°, 93°, b.p. 310°, 290°, 293° and 270°, respectively (Lucas, Ber. 21, 2510; Ipatiev, Ber. 41, 996; Goochot, Ann. chim. phys. [8], 12, 468). By catalytic hydrogenation of anthracene with the aid of a platinum catalyst, substances with the definite constitutions of 1,2,3,4-tetrahydroanthracene, or tetracene, m.p. 103–105°, and 1,2,3,4,5,6,7,8-octahydroanthracene, or octhracene, m.p. 73–74°, and a perhydride,  $C_{14}H_{24}$ , m.p. 61.5°, have been obtained (Schroeter, Ber. 57, 1990–2003; Fries, Ber. 65, 1494). For a perhydride of m.p. 89°, see Vol. II, p. 178.

*ms*-Alkyl-derivatives of dihydroanthracene are obtained by the reduction of alkyloxanthrones (p. 656). *ms*-Dialkyl-derivatives are obtained synthetically from alkylidene chlorides, benzene, and aluminium chloride. *ms*-Dimethyl-dihydroanthracene,  $C_6H_4(CH \cdot CH_3)_2C_6H_4$ , m.p. 181°, is obtained from ethylidene chloride, benzene, and aluminium chloride, and gives anthraquinone on oxidation (Anschütz, Ann. 235, 305, *et seq.*), in the same way as *as*-diphenylethane gives benzophenone. *ms* Diphenyl-dihydroanthracene, m.p. 153°, is obtained, together with triphenyl-methane, by the action of aluminium chloride and benzene on benzal chloride (Lineberger, Am. Chem. J. 13, 556). 9,9-Diphenyl-dihydroanthracene,  $(C_6H_5)_2C(C_6H_4)_2CH_2$ , m.p. 196°, is obtained by the reduction of diphenylanthrone (p. 653) with zinc dust in glacial acetic acid (Liebermann, Ber. 38, 1800).

Anthraquinone, or diketo-dihydroanthracene, is to be regarded as a derivative of dihydroanthracene. Anthrone and oxanthrone, which have already been considered in connection with anthranol and dihydroxyanthraquinone and their derivatives, are also members of the dihydroanthracene series.

Dihydroanthranol,  $C_6H_4 \begin{array}{c} \text{CH(OH)} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} C_6H_4$ , m.p. 76°, is obtained by reduction

of anthraquinone with zinc dust and ammonia. It readily decomposes, even on standing in the air, to water and anthracene. The alkyl-derivatives of dihydro-

anthranol,  $C_6H_4 \begin{array}{c} \text{CR(OH)} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} C_6H_4$ , are obtained by reduction of the alkyloxan-

thrones, or directly by the reduction of anthraquinone with zinc dust and caustic soda in the presence of alkyl halides. Like dihydroanthranol, they readily break down, even on heating with aqueous hydrochloric acid, into water and 9-alkyl-anthracenes (Liebermann, Ber. 18, 2150; Lineberger, Bull. [3], 6, 92; Liebermann, Ann. 212, 67). *ms*-Triphenylhydranthranol,  $(C_6H_5)_3C(C_6H_4)_2C(OH) \cdot C_6H_4$ , m.p. 200°, obtained by the action of phenyl magnesium bromide on diphenylanthrone (see above), gives triphenylhydranthracene,  $(C_6H_5)_3C(C_6H_4)_2 \cdot CHC_6H_4$ , m.p. 220°, on reduction. The latter is also obtained by treating the



condensation product of triphenylmethane-*o*-carboxylic ester and phenyl magnesium bromide with sulphuric acid (*Haller*, C.r. 139, 9).

**Phenylloxanthrone** is obtained by the oxidation of phenylanthrone (p. 653), and by the action of phenyl magnesium bromide on anthraquinone. A series of other *ms*-aryl- and *ms*-alkyl-anthracenes can be oxidised to the corresponding oxanthrones. Thus **tetramethyl-diamino-phenylloxanthrone**,

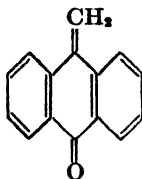
$$\begin{array}{c} \text{HO} \quad \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \quad \text{N}(\text{CH}_3)_2 \end{array} \text{CO} \quad , \text{ m.p. } 213^\circ$$
, is obtained from the condensation product of tetramethyl-diamino-diphenylmethane-*o*-carboxylic acid. It combines with dimethylaniline in the presence of phosphorus oxychloride to give the dye **phthalic green**, the chloride of the base,

$$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \quad \diagdown \\ \text{C}(\text{OH})[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2] \\ \diagdown \quad \diagup \end{array} \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \quad (\text{cf. p. 545}) \quad (\text{Haller, C.r. 137, 606})$$
,

of which **diphenyl-dihydroxy-dihydroanthracene**,  $\text{C}_6\text{H}_4[\text{C}(\text{OH})\text{C}_6\text{H}_5]_2\text{C}_6\text{H}_4$ , m.p.  $242^\circ$ , is the parent substance. This latter substance, which is obtained by the action of phenyl magnesium bromide on anthraquinone, condenses readily with phenols and aromatic amines to give tetra-aryl-dihydroanthracenes, in which respect it resembles *ms*-triphenyl-hydranthranol, both compounds being analogues of triphenylcarbinol (*Haller*, C.r. 138, 327; 140, 283). **Dimethyl- and diethyl-dihydroxy-dihydroanthracene**,  $\text{C}_6\text{H}_4[\text{C}(\text{R}(\text{OH}))_2\text{C}_6\text{H}_4]$ , m.p.  $181^\circ$  and  $175^\circ$ , respectively, are obtained from anthraquinone by the action of methyl- and ethyl-magnesium iodide (*Guyot*, Bull. [3], 33, 1144).

**1-Octracenone**, m.p.  $46-47^\circ$ , is obtained by the action of aluminium chloride on  $\gamma$ -2-tetralylbutyryl chloride (*Krollpfeiffer*, Ber. 56, 620).

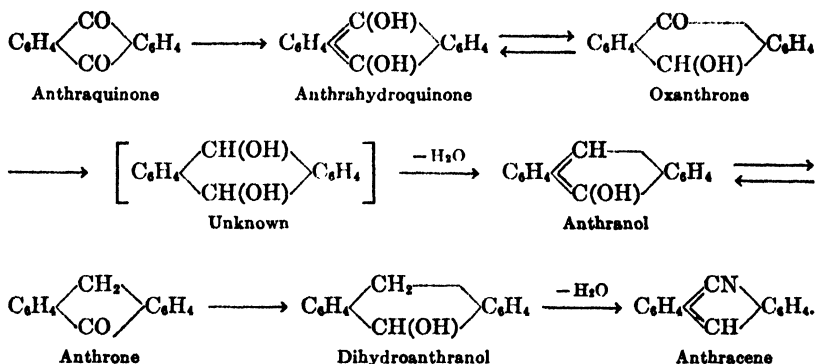
**Methylene-anthraquinone**,



has been obtained by the condensation of anthranol with formaldehyde. It forms yellow, stable prisms, m.p.  $148^\circ$  (*Meyer*, Ann. 420, 134). For other substituted methylene-anthraquinones, see *Padova*, Ann. chim. phys. [8], 19, 353.

**Anthraquinone**, diphenylene-diketone,  $\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}_4$ , m.p.  $285^\circ$ , b.p.  $382^\circ$ , forms yellow needles, which sublime. In addition to the usual synthetic methods given on p. 646 it is obtained very easily by the oxidation of anthracene with chromic acid mixture, and the latter can be regenerated by an electrolytic method (*Graebe*, Ann. Suppl. 7, 285). It can also be obtained from dihydroanthracene, *ms*-dichloro-, -dibromo-, -dinitro-, and -dimethyl-anthracene, and other meso-substituted anthracenes. In contrast to the isomeric phenanthraquinone, it is very stable towards oxidising agents. It combines with hydroxylamine to give anthraquinone-oxime, which sublimes above  $200^\circ$ , and can also be obtained by heating 9-nitroanthracene (p. 649) with methyl alcoholic potash. Unlike the true quinones, anthraquinone is not reduced by sulphur dioxide.

When heated with hydriodic acid or zinc dust and ammonia to  $150^\circ$ , it gives anthracene. By using different reducing agents, the intermediate stages of this reduction can be followed:



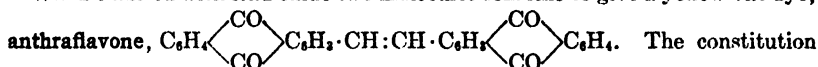
When anthraquinone is digested with zinc dust and sodium hydroxide solution, anthrahydroquinone is formed. When the red solution of this compound in alkalis is shaken with air, anthraquinone is regenerated (qualitative test for anthraquinone).

When reduced with zinc dust and alkali under pressure at 160°, two molecules combine and give dianthranol (p. 655).

When heated with caustic potash to 250°, anthraquinone breaks down into two molecules of benzoic acid. When heated with soda-lime it gives benzene and diphenyl, but with slaked lime, the principal product is diphenylene-ketone (*Anschtütz*, Ber. 18, 935).

**HOMOLOGUES OF ANTHRAQUINONE** are obtained by the synthetic methods, and also, in some cases, by oxidation of the alkyl-anthracenes. 1- and 2-Methyl-anthraquinone,  $\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}_3\cdot\text{CH}_3$ , m.p. 167° and 177°; 2-methyl-anthraquinone is also found in crude anthraquinone, and is obtained synthetically from *p*-toluyl-*o*-benzoic acid and sulphuric acid (*Limpriht*, Ann. 311, 180; *Heller*, Ber. 43, 2890). It is the volatile principle of theka wood (tectoquinone). (*Kafuku*, Bull. Chem. Soc. Japan 7, 114).

When oxidised with lead oxide two molecules combine to give a yellow vat dye,



of this compound has been arrived at by obtaining it by heating  $\omega$ -dibromo-methyl-anthraquinone with copper powder. Substituted anthraflavones have been obtained by similar processes (*Hepp*, Ber. 46, 709; *Ullmann*, Ber. 46, 712; *Ruggli*, Helv. 12, 71). Many methyl-anthraquinones are sensitive to light, but the constitution of the products is not known. In the presence of oxygen, they are oxidised to carboxylic acids (*Kasai*, J. Pharm. Soc. Japan 1927, No. 540, 15).

2,7-Dimethyl-anthraquinone, m.p. 170°; 2,3-dimethyl-anthraquinone, m.p. 208°. For other homologues of anthraquinone, see *Diels*, Ber. 62, 2337; *Morgan*, J. 1929, 2203; 2551; *Dougherty*, Am. 52, 1024.

Nuclear-hydrogenated anthraquinones have been obtained by the catalytic reduction of anthraquinone, with subsequent oxidation of the hydroquinones. Octahydro-anthraquinone, m.p. 183–184° (*Skita*, Ber. 58, 2687). For stereoisomeric forms of perhydrogenated anthraquinones, see *Alder*, Ann. 501, 247.

**SUBSTITUTED ANTHRAQUINONES.** Halogeno-anthraquinones are obtained: 1. by the action of chlorine or bromine on anthraquinone; 2. from chloro- and bromo-anthracenes by oxidation; 3. from amino-anthracenes through the diazonium compounds (*Kauffer*, Ber. 37, 59); 4. by the action of chlorine and bromine on anthraquinone- and anthracene-sulphonic acids in aqueous solution, the sulphonic acid group being readily exchanged for halogen (Ger. Pats. 205,195 and 228,876); 5. by synthesis from halogeno-benzophenone-*o*-carboxylic acids. 1-Chloro-, -bromo-, and -iodo-anthraquinones, m.p. 204°, 180°, and 177°, respectively; 2-chloro-, -bromo-, and -iodo-anthraquinones, m.p. 212°, 205°, and

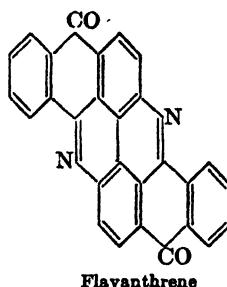
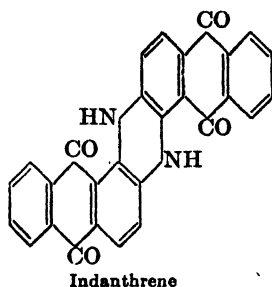
176°, respectively. When 2-bromo-anthraquinone, or the dibromo-anthraquinones are fused with potash, alizarin is formed (p. 662). Dibromo-anthraquinones are obtained by bromination of aminoanthraquinones, and subsequent removal of the amino-group. 1,3-Dibromo-anthraquinone, m.p. 210° (Ullmann, Ber. 49, 2154). For other compounds of this class, see *Grandmougin*, C.r. 173, 717, 839; *Battegay*, Bull. [4], 29, 1017. For trichloro-anthraquinones, see *Goldberg*, J. 1932, 73. Halogen atoms in the 1-position can readily be replaced by OH, OR, OC<sub>6</sub>H<sub>5</sub>, NH<sub>2</sub>, and NHR by heating with milk of lime, sodium alcoholate or phenate, ammonia, or amines (better with the addition of a copper salt).

When anthraquinone is boiled with antimony pentachloride and iodine, tetra- and heptachloro-anthraquinone are formed, with some octachloro-anthraquinone. Other perhalogenated anthraquinones have been obtained from halogenated benzoylbenzoic acids, or from halogenated phthalic anhydrides, halogenobenzenes and aluminium chloride (*Eckert*, Mo. 36, 269; *Hoffmann*, Mo. 36, 805; *Eckert*, J. pr. [2], 102, 361; *Fierz-David*, Am. 49, 2334). For polyiodo-anthraquinones, see *Eckert*, J. pr. [2], 121, 281.

**Nitroanthraquinones.**—When anthracene or anthraquinone is heated with nitric acid, 1-nitroanthraquinone, m.p. 230°, is formed, together with 1,5-dinitroanthraquinone, m.p. 385° (Ger. Pat. 167,699). Some 1,8-nitroanthraquinone, m.p. 312°, and the 1,6- and 1,7-dinitro-compounds are also formed (*Hefti*, Helv. 14, 1404). 2-Nitroanthraquinone, m.p. 185°, is obtained from 2-aminoanthraquinone by acting on the diazonium compound with potassium cupronitrite (cf. 2-nitronaphthalene, p. 614). It can also be obtained from 3-amino-2-nitroanthraquinone by eliminating the amino-group, and also synthetically from *o*-benzoyl-*p*-nitrobenzoic acid (*Scholl*, Ber. 37, 4435; *Kliegl*, Ber. 38, 295). By regulated alkaline reduction of the nitroanthraquinones, the relatively stable  $\beta$ -hydroxylamino-anthraquinones, C<sub>14</sub>H<sub>9</sub>O<sub>2</sub>(NHOH), C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>(NHOH)<sub>2</sub>, are formed. They isomerise with acids to aminohydroxy-anthraquinones (cf. p. 68) (*Wacker*, Ber. 35, 666). 2,2'-Azoxyanthraquinone, m.p. 343°, see *Scholl*, Mo. 32, 1035.

**AMINOANTHRAQUINONES.** The aminoanthraquinones and their derivatives are of outstanding importance in industry because substances like benzoylaminoanthraquinone and trianthraquinone-diimide are vat dyes, and other compounds, such as 2-aminoanthraquinone, can easily be converted into vat dyes by simple processes. Vat dyes are dyes insoluble in water and alkalis, which, on alkaline reduction—the so-called “vatting”—are converted into alkali-soluble hydro-compounds. These combine with the textile, and give the original dye on the thread by atmospheric oxidation. Vat dyes usually contain one or more CO groups, and it is on the capacity of these of passing into COH groups which are then capable of salt formation that the vatting process depends. Vat dyes are usually very fast (*Bohn*, Ber. 43, 987; *Staeble*, Chem. Ztg. 34, 731).

The aminoanthraquinones are produced: 1. by reduction of the nitroanthraquinones; 2. synthetically by condensation of aminobenzoyl-*o*-benzoic acids (Ger. Pat. 205,036); 3. nitro-, halogeno-, sulphonic acid, and hydroxyl groups in the  $\alpha$ - or 1-position in anthraquinone can be replaced by NH<sub>2</sub>, or NHR groups by heating with ammonia, amines, toluene sulphonamides, and particularly with aniline, best in the presence of copper powder (Ger. Pat. 126,392; *Dammann*, Z. Farben- und Textilchemie 1, 325; C. 1902, II, 368; *Battegay*, Bull. soc. ind. Mulhouse 87, 71; C. 1921, III, 408, etc.). For oxidation agents which can be used in this reaction, and avoid the production of sulphur dioxide, see *Lauer*, J. pr. [2], 135, 7. 1- and 2-Aminoanthraquinone form red needles, m.p. 252–253° and 302°, respectively; 2-aminoanthraquinone is converted into the interesting and useful vat dye indanthrene (*q.v.*) by fusing with potash at 250°, and under other conditions, e.g., by heating with aluminium chloride or antimony pentachloride in nitrobenzene solution, it gives the similarly constituted yellow flavanthrene (*q.v.*):

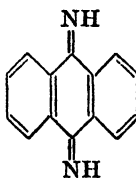


Di- and poly-aminoanthraquinones have been obtained by reduction of poly-nitro- or nitroaminoanthraquinones (see below) usually with sodium sulphide. 1,4-, 1,5- and 1,8-Diaminoanthraquinones melt at 268°, 319°, and 262° (Ger. Pat. 135,561; *Noelling*, Ber. 39, 637). 1,2-, 1,6-, and 1,7-Diaminoanthraquinones, m.p. 298°, 292°, and 290°. 1,2,3-triaminoanthraquinone, m.p. 328° (*Scholl*, Mo. 32, 1043). 1,2- and 2,3-Diamino- and 1,2,3-triaminoanthraquinone condense like *o*-phenylene diamine (p. 108) with *o*-dicarbonyl-compounds to give azines (*Scholl*, Ber. 47, 4531; Ger. Pat. 170,562).

Diazo-dyes prepared from 1,5-diaminoanthraquinone are substantive cotton dyes (*Maki*, J. Soc. Chem. Ind. Japan 34, 392).

As already mentioned, numerous acyl derivatives of the aminoanthraquinones, particularly benzoylaminoanthraquinones, are used directly as vat dyes. These compounds are obtained either by the action of benzoyl chloride on the aminoanthraquinones, or by the action of benzamide and copper powder on the halogenoanthraquinones. Benzoyl-1-aminoanthraquinone and dibenzoyl-1,5- and -1,8-diaminoanthraquinone give a yellow colour, the shade being displaced towards the red by substitution. Aminoanthraquinone derivatives of dicarboxylic acids, such as malonic acid, succinic acid, phthalic acid, etc., are vat dyes. They go under various trade names, such as algal yellow W.G., algal pink R, and algal scarlet G. Another series of vat dyes can be obtained from the aminoanthraquinones by heating them with a nitro-compound and concentrated sulphuric acid (*Bucherer*, Ber. 60, 2068). For urethane and urea derivatives of anthraquinone, see *Battegay*, Chimie et Ind. 8, 305, 307.

**ANTHRAQUINONE-DIIMIDES** are very stable compounds

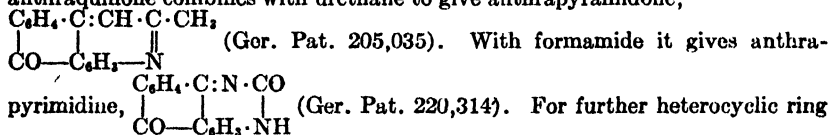


which are not hydrolysed even on long boiling with conc. hydrochloric acid. They are also very stable towards oxidising agents. Substituted anthraquinone-diimides are readily obtained by condensation of veratroyl nitrile, piperonyl nitrile, etc., with chlorosulphonic acid (*Keffler*, J. 119, 1476).

Dianthraquinone-imide,  $C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} C_6H_4 \cdot NH \cdot C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} C_6H_4$ , and trianthraquinone-diimide,  $A-NH-A-NH-A$ , are obtained by condensation of mono- and di-aminoanthraquinones with halogeno-anthraquinones by heating the components with sodium acetate in nitrobenzene solution, best with the addition of copper powder (Ger. Pat. 162,824). Many of these substances, as for example, the products obtained from 1,5-diamino- and 2-chloroanthraquinone, and from 1,5-dichloro- and 2-aminoanthraquinone, are dyes, though some have to be treated in various ways before acting as vat dyes. Some trade names of these

dyes are indanthrene bordeaux B, indanthrene red G, algal orange R, algal bordeaux 3B, and algal red P.

1-Aminoanthraquinone, like *o*-aminobenzaldehyde (p. 280), and *o*-aminoacetophenone (p. 286), is capable of forming heterocyclic ring-systems, the addition taking place in the 1,9-position in the anthraquinone nucleus. Thus, with acetone and caustic soda, an *o*-methyl-anthrapyridine, is formed, analogous to the formation of quinaldine from *o*-aminobenzaldehyde (Ger. Pat. 185,548). 1-Aminoanthraquinone combines with urethane to give anthrapyridone,



formations see *Danmann*, Z. Farben-und Textilchemie 1, 325; Ger. Pats. 171,293 and 203,752.

The action of nitric acid on the free aminoanthraquinones gives rise to the very stable nitroaminoanthraquinones (p. 111, and *Scholl*, Ber. 37, 4434). The simplest, 1-nitroaminoanthraquinone,  $\text{C}_{14}\text{H}_7\text{O}_2 \cdot \text{NHNO}_2$ , forms yellow needles, m.p. 193° (decomp.), and is obtained by oxidation of 1-anthraquinone diazonium sulphate with sodium hypochlorite (Ger. Pat. 156,803). The nitration of acetyl-compounds and the urethanes of aminoanthraquinones proceeds smoothly. *p*-Nitro-compounds are obtained first, mainly, and then *o*-nitro- and *o,p*-dinitroaminoanthraquinones (Ger. Pat. 171,588). For the nitration and bromination of the aminoanthraquinones, see *Lauer*, J. pr. [2], 136, 1.

When brominated, 1-aminoanthraquinone gives 2-bromo- and 2,4-dibromo-1-aminoanthraquinone, m.p. 181° and 222°. 2-Aminoanthraquinone gives 1,3-dibromo-2-aminoanthraquinone (*Scholl*, Ber. 40, 1701; Ger. Pat. 160,169; *Jung-haus*, Ann. 399, 316; *Ullmann*, Ann. 399, 330). 2-Bromo-1-aminoanthraquinone is of special interest because it can be converted into indanthrene by heating with sodium acetate in nitrobenzene solution, in the presence of copper chloride (Ger. Pat. 158,287).

1,3-Dichloro-2-aminoanthraquinone, 3-bromo-1-amino- and 2-bromo-1-aminoanthraquinone, m.p. 243° and 182°; 2-bromo-1,4-diaminoanthraquinone, m.p. 234°; 2,4-dibromo-1-aminoanthraquinone, m.p. 222° (*Ullmann*, Ber. 49, 2154).

**ANTHRAQUINONE-DIAZIDES** are obtained by the action of ammonia on the perbromides of the corresponding diazonium salts. The 1-diazides are unstable and readily split off nitrogen, but the 2-diazides appear to be more stable (*Brass*, Ber. 61, 983).

**ANTHRAQUINONE SULPHONIC ACIDS.** When anthraquinone is heated with fuming sulphuric acid the chief product is 2-anthraquinone sulphonic acid, but some 1-anthraquinone sulphonic acid is also formed. On further sulphonation 2,6- and 2,7-anthraquinone disulphonic acids are formed. If some finely powdered mercuric salt is added to the sulphonating mixture, the formation of 1-anthraquinone monosulphonic acid is favoured, together with some 1,5- and 1,8-disulphonic acid. The sulphonic acid group enters in each case first in the 1-position, but without the addition of the mercuric salt, the sulphonation temperature is so high that most of the 1-acid is converted into the 2-acid (*Martinet*, C. 1921, III, 224; *Lauer*, J. pr. [2], 135, 164, 182). Chlorinated and brominated anthraquinone sulphonic acids are obtained by sulphonating the corresponding substituted anthraquinones (*Fierz-David*, Helv. 10, 197; *Schilling*, Ber. 46, 1066). On illumination of hydrochloric acid solutions of the anthraquinone sulphonic acids, the sulphonic acid group is replaced, more or less completely, by chlorine (*Eckert*, Ber. 60, 1691). 1-Anthraquinone-monosulphonic acid when further sulphonated in the absence of a mercuric salt, gives 1,6- and 1,7-disulphonic acids. Sulphonic acid groups in the 1- (or  $\alpha$ -) position are readily replaced by  $\text{NH}_2$  or  $\text{NHR}$  by heating with ammonia or amines, by  $\text{CH}_3\text{O}$  or  $\text{C}_6\text{H}_5\text{O}$  groups by heating with methyl alcoholic alkali or potassium phenate, and by OH groups by heating with milk of lime under pressure (*Iljinski*, Ber. 36, 4194; *Schmidt*, Ber. 37, 66; *Dunachmann*, Ber. 37, 331; *Liebermann*, Ber. 37, 646). The sulphonic acids, particularly those with the sulphonic acid group in the 2-position, give the following products (together with higher hydroxylated products) when fused with potash:

- 2-Anthraquinone-monosulphonic acid  $\begin{cases} \rightarrow \text{2-Hydroxyanthraquinone} \\ \rightarrow \text{Alizarin (1,2 OH)} \end{cases}$
- 2,6-Anthraquinone-disulphonic acid  $\begin{cases} \rightarrow \text{Anthraflavinic acid (2,6 OH)} \\ \rightarrow \text{Flavopurpurin (1,2,6 OH)} \end{cases}$
- 2,7-Anthraquinone-disulphonic acid  $\begin{cases} \rightarrow \text{Isoanthraflavinic acid (2,7 OH)} \\ \rightarrow \text{Anthrapurpurin (1,2,7 OH), etc.} \end{cases}$

The sulphonic acids of the amino-, alkylamino- and arylamino-anthraquinones are in some cases valuable dyes, e.g., alizarin saphirol,

$\text{NH}_2[8]\text{SO}_3\text{H}[6]\text{OH}[5]\text{C}_6\text{H} \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}_6\text{H}[1]\text{OH}[2]\text{SO}_3\text{H}[4]\text{NH}_2$ , obtained by reduction of dinitroanthrarufin-disulphonic acid; alizarin pure blue,

$\text{C}_6\text{H}_2 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}_6\text{H}[1]\text{NH}_2[2]\text{Br}[4]\text{NHC}_6\text{H}_5\text{SO}_3\text{H}$ , alizarin cyanine green, anthra-

quinone green, and many others. The method of preparation is usually to act on 1-halogeno-, 1-nitro-, or 1-hydroxy-anthraquinones with ammonia, aliphatic or aromatic amines, and then sulphonate the product (*Buntrock*, Ber. 34, 2344. *Friedländer*, Z. Farben- und Textilchemie 3, 218).

For the bibliography of anthraquinone sulphonic acids, and their derivatives, see Chem. Ind. 32, 477. For the separation, identification, and quantitative determination of anthraquinone sulphonic acids, see *Lauer*, J. pr. [2], 130, 185. For the polysulphonation of anthraquinone, see *Lauer*, J. pr. [2], 135, 361.

**HYDROXYANTHRAQUINONES.** The hydroxyanthraquinones are obtained (1) from bromo- and chloro-anthraquinones, or anthraquinone sulphonic acids by fusion with alkali, or heating with milk of lime. The substituents are first replaced by OH, but at higher temperatures, in the case of the fusion with potash, oxidation occurs, and further OH groups enter. Anthraquinone monosulphonic acid gives mono- and di-hydroxyanthraquinones. The latter is also obtained by fusing hydroxyanthraquinone with alkali (*Liebermann*, Ber. 11, 1613) and by fusing nitroanthraquinones with acid potassium acetate at 170–180° (*Schwenk*, J. pr. [2], 103, 106). (2) Hydroxyanthraquinones can be obtained synthetically from phthalic anhydride and phenols, from *m*-hydroxybenzoic acids (p. 646) by heating with sulphuric acid, and from hydroxybenzoyl-*o*-benzoic acids (*Bentley*, Proc. 24, 52; J. 93, 435).

If hydroxyanthraquinones are heated with fuming sulphuric acid, preferably with the addition of boric acid, additional hydroxyl groups enter the molecule. It is usually H atoms in the  $\alpha$ -position of the unsubstituted ring that are replaced by OH. Thus, 1-hydroxyanthraquinone gives 1,5-dihydroxyanthraquinone, and alizarin gives 1,2,5-trihydroxy- and 1,2,5,8-tetrahydroxy-anthraquinone. Anthraquinone itself can be converted into hydroxyanthraquinones by this method (preparation of quinizarin) (*Wacker*, J. pr. [2], 57, 88).

By long fusion with alkali, the hydroxyanthraquinones break down to hydroxybenzoic acids, in the same way as anthraquinone breaks down into benzoic acid. This reaction can be used to determine the constitution of a hydroxyanthraquinone (*Liebermann*, Ber. 12, 1293; *Offermann*, Ann. 280, 1).

The hydroxyanthraquinones are reduced to anthracene by heating with zinc dust. Individual hydroxyl groups can be reduced by heating with stannous chloride and caustic soda (*Liebermann*, Ann. 183, 216). On heating with aqueous ammonia, to 150–200°, individual OH groups are substituted by amino-groups.

In the etherification of hydroxyanthraquinones, certain rules can be formulated



monobromo-anthraquinone, from the two hydroxyanthraquinones, and from anthraquinone sulphonic acid, by fusion with potash. Anthracene itself can be converted into alizarin by fusion with alkali and sodium chlorate (Ger. Pat. 186,526).

In the industrial preparation, anthraquinone prepared from purified (50%) anthracene is used. It is converted into 2-anthraquinone monosulphonic acid by fuming sulphuric acid. This is then submitted to prolonged fusion with caustic soda at 180–200° under pressure, and with the addition of potassium nitrate or chlorate as oxidising agent. In this way sodio-alizarin is obtained, which is decomposed by hydrochloric acid, and is put on the market as a 10–20% paste.

Alizarin is also obtained by heating phthalic anhydride with catechol and sulphuric acid. The isomeric hystazarin is obtained at the same time. It is also prepared from phthalic anhydride and *o*-dichlorobenzene in the presence of aluminium chloride, followed by fusion with potash (*Phillips*, Am. 49, 473).

Alizarin dissolves readily in alcohol and in ether, but is difficultly soluble in hot water. It dissolves in alkalis with a purplish-red colour. Calcium and barium hydroxides precipitate the corresponding salts from this solution, as blue compounds. Aluminium and tin salts give red, ferric salts, blackish-violet, and chromium salts violet-brown precipitates (alizarin lakes, see p. 662).

In cotton dyeing and printing the red aluminium lake, and the almost black iron lake are usually used. In the case of wool, the aluminium and chromium lakes are most often used. The fabric, mordanted with alumina, is heated with alizarin suspended in water, when alizarin aluminate is fixed on the thread. In dyeing with Turkey red oil, sulphonated castor oil, the fabric is mordanted with the oil and alum. The alumina then combines with both the oil and the alumina.

On prolonged fusion with alkali, alizarin is broken down into benzoic and proto-catechuic acids.

**Alizarin dimethyl ether**,  $C_{14}H_8O_2(OCH_3)_2$ , m.p. 215°, is obtained by oxidation of 1,2-dimethoxyanthrone, or by heating 1-nitro-2-methoxyanthraquinone with methyl alcoholic potash. When hydrolysed with concentrated sulphuric acid it gives **alizarin-2-monomethyl ether**, m.p. 230°, a compound which can also be obtained by direct methylation of alizarin (p. 662, and Ann. 349, 201). The isomeric **alizarin-1-monomethyl ether**, m.p. 179°, which has not yet been obtained synthetically, is found, together with hystazarin monomethyl ether and anthragallol-1,2- and 1,3-dimethyl ethers, in the root of *Oldenlandia umbellata* (*Perkin*, Proc. 23, 288; J. 91, 2066).

**3-Nitro-alizarin**, *alizarin orange*,  $C_6H_4(CO)_2C_6H(OH)_2[3]NO_2$ , forms orange-red leaflets, m.p. 244°, and is obtained from alizarin by nitration in acetic acid solution, or by the action of nitrous fumes. It is used industrially, its aluminium lake being coloured orange. **3-Amino-alizarin**, obtained by reduction of 3-nitro-alizarin, forms an anhydro-base with acetic anhydride, which contains the  $NH_2$  group in the ortho position to an OH group (*Roemer*, Ber. 18, 1666; *Schultz*, Ber. 35, 906). On heating with glycerol, nitrobenzene, and sulphuric acid (*Skraup's* synthesis of quinoline) it gives alizarin blue, a derivative of anthraquinoline (*Brunner*, Ber. 18, 447). The isomeric **4-nitro-alizarin**,  $C_6H_4(CO)_2C_6H(OH)_2[4]NO_2$ , m.p. 195°, is obtained by nitrating diacetyl-alizarin (*cf. Brasch*, Ber. 24, 1610). **4-Amino-alizarin**, obtained by reduction, gives a green dye, alizarin green, isomeric with alizarin blue, when treated with glycerol, nitrobenzene, and concentrated sulphuric acid.

**1-Hydroxy-2-aminoanthraquinone**, alizarin amide,  $C_{14}H_8O_2(OH)NH_2$ , m.p. 225°, is obtained by heating alizarin with aqueous ammonia to 200° (*Scholl*, Ber. 39, 1201).

**Aminohydroxyanthraquinones** can also be obtained from hydroxylamino-anthraquinones (obtained by reduction of nitroanthraquinones) by isomerisation with sulphuric acid (*cf. p. 68*) (*Schmidt*, Ber. 29, 2934; *Wacker*, Ber. 35, 666),



and by the action of fuming sulphuric acid on amino- and alkylamino-anthraquinones (Ger. Pat. 154,353). **Bromo-alizarin**, see *Liebermann*, Ber. 33, 1664. **Halogenated alizarins** have been prepared in large numbers via the sulphonic acids (*Heller*, Ber. 46, 2703). **Alizarin sulphonic acids**, see Ger. Pat. 210,863.

Three of the dihydroxyanthraquinones isomeric with alizarin contain the OH groups in one benzene nucleus (isonuclear):

(1,3)-**Purpuroxanthin**, obtained from resorcinol and phthalic anhydride; (1,4)-**quinizarin**, from hydroquinone, and (2,3)-**hystazarin**, from catechol (Ber. 28, 116). They are better obtained from their ethers, which are obtained by the condensation of the corresponding dihydroxybenzene ethers and phthalic anhydride in the presence of aluminium chloride (*Lagodzinski*, Ann. 342, 99). Quinizarin is formed by the action of concentrated sulphuric acid and nitrous acid on anthraquinone or 1-hydroxyanthraquinone. The sulphate of 1-hydroxy-4-diazoanthraquinone can be isolated as an intermediate product. On stronger heating with sulphuric acid it is converted into quinizarin and nitrogen (Ger. Pat. 161,954). An interesting method of formation of quinizarin is from the action of 1,4-naphthohydroquinone and maleic anhydride, which gives it the structure of a 9,10-dihydroxy-1,4-anthraquinone (*Zahn*, Ann. 462, 72). Hystazarin is obtained industrially by the oxidation of anthraquinone with fuming sulphuric acid in the presence of boric acid. On prolonged heating with sulphuric acid it partially isomerises to alizarin (*Liebermann*, Ber. 35, 1778). For derivatives of hystazarin, see *Schrobsdorff*, Ber. 36, 2936. **Quinazarin monosulphonic acid**, *rufanic acid*, is used as a precipitant for bases (*Zimmermann*, Z. physiol. Chem. 188, 180).

The following dihydroxyanthraquinones, which contain the OH groups in different benzene rings (heteronuclear), are usually obtained from the corresponding disulphonic acids, by heating with milk of lime:

(1,5)-**Anthrarufin**, 1,6- and 1,7-dihydroxyanthraquinone, (1,8)-**chrysazin**, (2,7)-**isoanthraflavinic acid**, (2,6)-**anthraflavinic acid**. These are obtained, together with 1,5- and 1,7-dihydroxyanthraquinones by condensation of *m*-hydroxybenzoic acid. Chrysazin (derivatives, see *Wöbling*, Ber. 36, 2941) is also obtained from its tetranitro-compound, **chrysaminic acid**,  $C_{14}H_5(NO_2)_4(OH)_2O_2$ , by reduction and elimination of the amino-groups. Chrysaminic acid is obtained by heating aloes with concentrated sulphuric acid. For the spectra of dihydroxyanthraquinones, see *Liebermann*, Ber. 19, 2327.

**Homologues of the dihydroxyanthraquinones**.—1,8-Dihydroxy-3-methylanthraquinone,  $C_{14}H_5(CH_3)O_2(OH)_2$ , is **chrysophanic acid**, m.p. 196° (*Hesse*, Ann. 284, 193; *Oesterle*, Arch. Pharm. 243, 434; *Léger*, C.r. 154, 281), which is present in senna leaves from species of *Cassia*, and in the rhubarb root from species of *Rheum*, together with methyl-chrysophanic acid (*Hesse*, Ann. 309, 32). Chrysophanic acid is obtained synthetically by condensation of *o*-nitrophthalic anhydride with *m*-cresol, whereby a substituted benzoyl-benzoic acid is formed. The nitro-group is then replaced by hydroxyl, and the ring closed (*Eder*, Helv. 5, 3). For another synthesis, see *Naylor*, Am. 53, 4114.

**Chrysarobin**,  $C_{18}H_{12}O_4$ , is chrysophanic acid-9-anthrone (*Naylor*, Am. 53, 4114). It is found in goa and araroba powder, an exudation from dye and Brazilian trees, and is used in pharmacy as a vesicant (*Liebermann*, Ber. 21, 447). It is readily oxidised in the air, and in the organism to chrysophanic acid. Besides chrysarobin, goa powder contains chrysophanic acid-anthranol, emodin-anthranol-methyl ether, emodin monomethyl ether, and emodin (p. 665) (*Eder*, Arch. Pharm. 254, 1; *Hesse*, Ann. 388, 65).

The so-called **methyl-alizarin**, m.p. 251°, is isomeric with chrysophanic acid. It is obtained from methyl-anthraquinone sulphonic acid, and behaves very similarly to alizarin. Various **methyl-purpuro-xanthines** have been prepared by condensation of 1,3,5-dihydroxybenzoic acids with *o*- and *m*-toluic acids (*Schunck*, J. 69, 68). A methyl alizarin, m.p. 216°, and a methyl-hystazarin,  $(OH)_2[6,7]-C_6H_2(CO)_2C_6H_3[2]CH_3$ , are obtained by condensation of 5-methyl-phthalic acid with catechol (*Niemcewiczski*, Ber. 33, 1629). **Dimethyl-anthrarufin**,  $(CH_3)(OH)C_6H_2(CO)_2C_6H_3(CH_3)(OH)$ , is obtained by the action of sulphuric acid on *sym*-hydroxytoluic acid (*Jowett*, J. 83, 1331).

For rubiadin and nataloin, see Vol. II, pp. 428, 430.

**Shikizarin**, m.p. 232°, is 1-methyl-5,8-dihydroxy-anthraquinone, and is obtained by heating shikonin (*Majima*, Acta phytochim. 1, 43). For other homologues of alizarin, see *Bradburg*, J. 105, 2748.

(c) *Trihydroxyanthraquinones* are obtained by fusing anthraquinone disulphonic acids (p. 660) or mono- or dihydroxyanthraquinones, with alkali or other oxidising agents. They can readily be built up from derivatives of naphthaquinone (*Dimroth*, Ann. 411, 339).

**Purpurin**,  $C_6H_4(CO)_2C_6H[1,2,4](OH)_3 + H_2O$ , m.p. 253° (anhydrous), can be sublimed, is found together with alizarin in madder root. It is formed from alizarin and quinizarin by heating with manganese dioxide and sulphuric acid to 150°, and from tribromoanthraquinone. It can be obtained synthetically from phthalic anhydride, and 2,4-dibromophenol, followed by fusion with alkali (*Tunaka*, Proc. Imp. Acad. Tokyo 3, 345). Purpurin dissolves readily in hot water, alcohol, ether, and alkalis, with a pure red colour. Lime water and baryta water precipitate purplish-red compounds. It produces a beautiful scarlet colour with mordanted fabrics.

When purpurin is heated with aqueous ammonia to 150°, **purpurinamide**,  $C_{14}H_8O_2(NH_2)(OH)_2$ , is formed.

**Anthragalol**, (1,2,3) (derivatives, see *Bamberger*, Mo. 22, 717; Mo. 23, 688; *Bock*, Mo. 23, 1008; 26, 571), anthra- or isopurpurin (1,2,7), and **flavopurpurin** (1,2,6) (*Frobenius*, Ber. 40, 1048), **hydroxychrysazine** (1,2,8), **hydroxyanthraquinone** (1,2,5) (*Graebe*, Ann. 349, 215), and 1,4,8-trihydroxyanthraquinone (Ger. Pat. 163,041), are isomeric with purpurin. The first three are used industrially in dyeing and printing. For the determination of the constitution of these substances by fission of the sulphonic acids related to them, see *Offermann*, Ann. 280, 1. 1,3,8-Trihydroxyanthraquinone, m.p. 278°, forms bright red needles.

*Homologous trihydroxyanthraquinones*:—Trihydroxy-methylantraquinones are obtained by the condensation of dimethoxy-phthalic anhydrides with *o*-, *m*- and *p*-cresol in the presence of aluminium chloride (*Graves*, Am. 45, 2439; *Simonsen*, J. 125, 721; *Keimatsu*, J. Pharm. Soc. Japan, 49, 158; 50, 61). **Emodin**, or frangula-emodin,  $(HO)_2C_6H_2(CO)_2C_6H_2(OH)CH_3$ , m.p. 255°, is a 1,6,8-trihydroxy-3-methyl-anthraquinone (see Vol. II, p. 429). **Aloe-emodin**, a 3-(hydroxymethyl)-1,8-dihydroxyanthraquinone, m.p. 224°, is isomeric with it. It is obtained from **barbaloin** (Vol II, p. 364) by hydrolysis with dilute hydrochloric acid. Oxidation with chromic acid converts it into 1,8-dihydroxyanthraquinone-3-carboxylic acid, a substance called **rhein**, which has also been isolated from Chinese rhubarb (Vol. II, p. 429). Isomeric with emodin is **morindone**, m.p. 280–282°, which is obtained by hydrolysis of morindin, the glucoside present in *Morinda citrifolia*. It is a 1,2,5-trihydroxy-6-methylantraquinone, and can be obtained synthetically by condensation of opianic acid with *p*-bromocresol, reduction of the phthalide formed with zinc and caustic soda, and ring-closure with 85% sulphuric acid. The anthrone derivative obtained is converted into morindone through morindone-dimethyl ether (*Jacobson*, Am. 47, 283; *Bhattacharya*, J. Indian Inst. Sci. 10, A 6; Vol. II, p. 430). **Chrysarone**, 3,5,6-trihydroxy-2-methyl-anthraquinone (*Keimatsu*, J. Pharm. Soc. Japan, 49, 63). **Isoemodin**, 3,5,8-trihydroxy-2-methyl-anthraquinone (*Keimatsu*, J. Pharm. Soc. Japan 49, 20). **Helminthosporin**, see Vol. II, p. 429.

(d) *Tetra- and poly-hydroxyanthraquinones* are obtained by heating hydroxyanthraquinones with fuming sulphuric acid, best with addition of boric acid (cf. p. 661, and *Schmidt*, J. pr. [2], 43, 231; 44, 103). In this way, **quinizarin**, or alizarin bordeaux,  $C_{14}H_8O_5[1,2,5,8](OH)_4$ , is obtained from alizarin. When it is oxidised with manganese dioxide and sulphuric acid it forms **alizarin-pentacyanine**,  $C_{14}H_8O_5(OH)_4$ , 1,2,4,5,8-pentahydroxyanthraquinone, a blue mordant dye (Ger. Pats. 66,153 and 119,756). An anthraquinone,  $(HO)_2C_6H(CO)_2C_6H_2O_5$ , is formed intermediately. Two isomeric tetrahydroxyanthraquinones, **anthrachrysone** and **rufiopin** are formed from *sym*-dihydroxybenzoic acid (p. 367) and from opianic acid (p. 381) or protocatechuic acid (p. 365) and sulphuric acid. **Rufiopin** is a 1,2,5,6-tetrahydroxyanthraquinone, which can be synthesised in the same way as morindone (*Puntambeker*, Am. 49, 486). When gallic acid is heated with sulphuric acid, **rufigallic acid**,  $C_{14}H_8O_5[1,2,3,5,6,7](OH)_6$ , is formed. It is a hexahydroxyanthraquinone, which dissolves in alkalis with a blue colour,

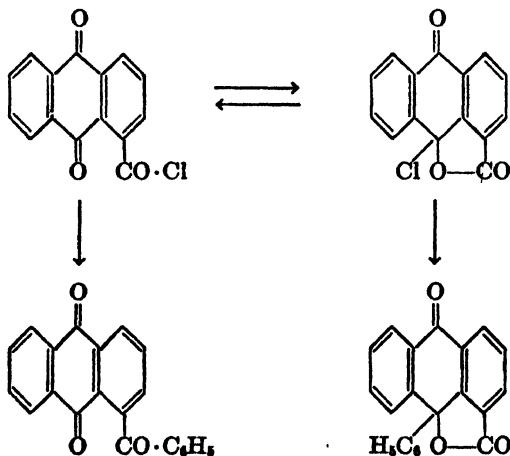
and dyes fabrics mordanted with chromium a brown colour. It comes on the market in combination with anthrapurpurin as alizarin- or anthracene-brown. Anthracene blue is an isomeric hexahydroxyanthraquinone, which is obtained by the action of fuming sulphuric acid on dinitroanthraquinone, and is a 1,2,4,5,6,8-hexahydroxy-anthraquinone. Kermesic acid, carminic acid, and probably laccic acid, are to be regarded as tetrahydroxyanthraquinones. They are dealt with under the natural dyes in Vol. II, p. 430.

A review of the naturally occurring anthraquinone derivatives is given by Mitter, J. Indian Chem. Soc. 5, 769.

**ANTHRAQUINONE-CARBOXYLIC ACIDS:** 1- and 2-Anthraquinone carboxylic acids are obtained by oxidation of the anthracene carboxylic acids. The 1-acid (m.p.  $285^{\circ}$ ) is also obtained by condensation of benzoyl-phthalic acid and isophthalic acid (Graebe, Ann. 290, 217). The 2-acid (m.p.  $291^{\circ}$ ; Limpricht, Ann. 311, 182) is obtained by the action of chromic acid on methyl-anthracene or methyl-anthraquinone. The amide of the 1-acid gives 1-amino-anthracene when treated with bromine and alkali (p. 658; Graebe, Ber. 30, 1115), and the acid itself can be obtained from this through the nitrile (Ullmann, Ann. 388, 200). 1,5-Anthraquinone dicarboxylic acid, m.p.  $326^{\circ}$ , is obtained in a similar way (Scholl, Ber. 62, 107). Other anthraquinone dicarboxylic acids are obtained by the oxidation of the corresponding dimethylantraquinones. Anthraquinone-2,7-dicarboxylic acid, m.p. above  $360^{\circ}$ ; anthraquinone-1,2-dicarboxylic acid, m.p.  $267-268^{\circ}$ , with anhydride formation. These substances serve as the starting point for the preparation of more highly condensed systems, which will be described later (see p. 708). Munjistin, 2,4-dihydroxyanthraquinone-3-carboxylic acid, is found in some species of madder (Vol. II, p. 428).

Trihydroxyanthraquinone-carboxylic acid, purpurin-carboxylic acid,  $C_{14}H_4O_7$  (OH) $_3$ COOH, is the so-called pseudopurpurin, which is found in crude purpurin from madder root, and on heating breaks down into carbon dioxide and purpurin. For synthetic purpurin carboxylic acids, see Perkin, J. 65, 842. 1-Nitroanthraquinone-carboxylic acid is used as a reagent for the identification of alcohols (Sah, J. Chin. Chem. Soc. 1, 51).

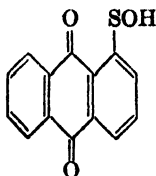
The chlorides of the anthraquinone-carboxylic acids give 1- and 2-benzoyl-anthraquinones, when treated with benzene and aluminium chloride (Schaarschmidt, Ber. 48, 831). In addition to the ketones, isomeric lactones are also formed. Their formation is explained by tautomerism of the anthraquinone carboxylic chlorides (Scholl, Ann. 493, 56; 494, 201; 512, 1, 30, 112), e.g.:



Mercaptans and mercapto-derivatives of anthraquinone are formed by the action of potassium hydrosulphide or mercaptans on halogeno- and nitro-anthraquinones (Gattermann, Ann. 393, 113). Mercaptan-anthraquinones can also be obtained by the hydrolysis of the corresponding thiocyanates with alcoholic potash; the thiocyanates are readily obtained from aminoanthraquinones by diazo-

tising and boiling with potassium thiocyanate. The mercaptan-anthraquinones very readily oxidise and pass into the disulphides. Anthraquinone-2-mercaptan, yellow needles, m.p. 206°; methyl ether, m.p. 162°. Ring closure readily occurs when these substances are treated with dehydrating agents, and thiazole- and thiophene derivatives are formed (Gattermann, Ann. 393, 113). The reaction of *o*-halogeno-amino-anthraquinones with potassium thiobenzoate leads directly to anthraquinone-thiazole derivatives, which are used as dyes (Ullmann, Ann. 399, 345).

#### Anthraquinone-sulphenic acid

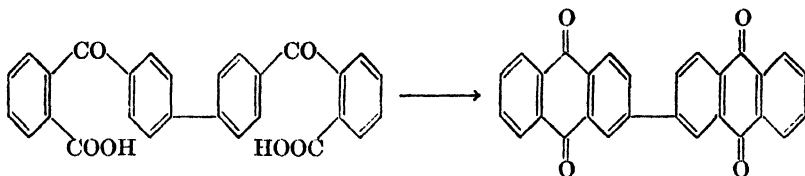


can be obtained by the action of halogens on the mercaptans. The "sulphochloride" first formed is converted into an alkoxy-compound, and is then hydrolysed. It is a bright red substance and is acidic. *ms*-Dithioanthraquinone, see Heilbron, J. 123, 173.

**OTHER ANTHRACENE-QUINONES:** Besides 9,10-anthraquinone, 1,2- and 1,4-anthraquinones are known. 1,2-Anthraquinone forms orange needles, m.p. 160°, and is obtained by oxidation of 1-hydroxy-aminoanthracene (Lagodevski, Ber. 27, 1438; Ann. 342, 80). 1,4-Anthraquinone, yellow needles, m.p. 218°, is obtained by oxidation of 1,4-diamino-anthracene with ferric chloride (Liebermann, Ber. 41, 1436). 2-Hydroxy-1,4-anthraquinone, see Fieser, Am. 50, 465.

**ANTHRA-DIQUINONES** have been prepared by oxidation of hydroxy- and polyhydroxy-anthraquinones. Hystazarinquinone, 2,3,9,10-anthra-diquinone, obtained from hystazarin by the action of lead tetracetate, forms bronze coloured needles, decomposing at 315° (Tanaka, Chem. News 131, 20). Quinizarinquinone, 1,4,9,10-anthra-diquinone, straw-yellow needles, m.p. 211-213° (Dimroth, Ann. 411, 345; Lesser, Ber. 47, 2526). Hydroxyanthra-diquinones and anthratriquinones, see Dimroth, Ber. 54, 3050; Schmidt, Ber. 62, 1884.

**DIANTHRAQUINOYLS.** These are compounds in which two anthraquinone radicals are linked directly with each other in the 1- or 2-position. They are produced in the same way as diphenyl (p. 493): (1) from iodo- or chloro-anthraquinones, by heating with copper powder; (2) from the anthraquinone diazonium sulphates with acetic anhydride and copper powder (Scholl, Ber. 40, 1697; Ger. Pat. 215,006). (3) They may be obtained by a method analogous to the synthesis of anthraquinone. Diphenyl and phthalic anhydride are heated in the presence of aluminium chloride, giving diphenyl-diphthaloylic acid, which is then treated with dehydrating agents (Scholl, Ber. 44, 1075):



Derivatives of dianthraquinoyl have also been obtained by oxidation of hydroxy-anthraquinone, and by condensation of 1,2-anthraquinone with sulphuric acid (Eckert, Ber. 60, 1693).

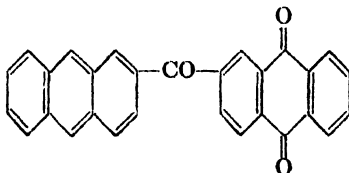
1,1'-Dianthraquinoyl, brownish-yellow prisms, m.p. 435°, is obtained by methods (1) and (2). 2,2'-Dianthraquinoyl, m.p. 388°, is obtained by methods (1), (2), and (3). 2,2'-Dimethyl-1,1'-dianthraquinoyl, m.p. 367°; 2,4,2',4'-tetramethyl-1,1'-dianthraquinoyl, m.p. 297° (Scholl, Ber. 43, 512).

4,4'-Dimethyl-1,1'-dianthraquinoyl, rhombic tablets with a yellow colour, m.p. 386° (Ullmann, Ber. 45, 687).

1,1'-Dianthraquinoyl-2,2'-dicarboxylic acid is obtained by oxidation of 2,2'-dimethyl-1,1'-dianthraquinoyl. Like the *o,o'*-disubstituted diphenic acids (p. 495) it has been resolved into optical isomers (*Kuhn*, *Ann.* **464**, 91). For hydroxy-dianthraquinoyls, see *Seer*, *Mo.* **34**, 631; *Scholl*, *Ber.* **52**, 2254.

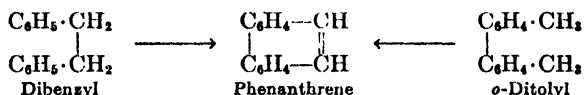
1,1'-Dianthraquinoyls give a cherry-red solution with concentrated sulphuric acid, which becomes dark green on addition of copper powder. The reaction is characteristic for these compounds (*Seer*, *Mo.* **34**, 633).

Ketones in which an anthracene nucleus is linked with an anthraquinone nucleus by a CO bridge can be obtained by condensation of 1- and 3-chloroanthraquinone-2-carboxylic chloride with anthracene. The type of compound is illustrated by the formula (*de Diesbach*, *Helv.* **15**, 1241):

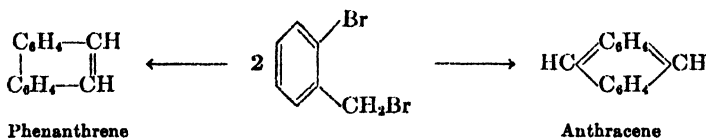


#### 4. PHENANTHRENE GROUP

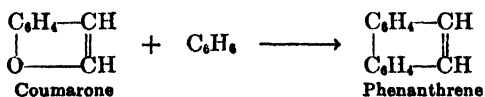
**Phenanthrene** is found in coal-tar, together with anthracene (p. 645). It is also found with fluoranthene (p. 689) and pyrene in a product obtained by distilling a mercury ore from idrialite. In a more or less hydrogenated form, the phenanthrene molecule forms the basis of a number of important naturally occurring substances, and for this reason, is of special importance. It is obtained synthetically: (1) together with diphenyl, anthracene, and other hydrocarbons by passing the vapours of various benzene derivatives through a red-hot tube. Thus, toluene, stilbene, diphenyl and ethylene, and particularly dibenzyl, and *o*-ditolyl, give phenanthrene when treated in this manner:



(2) By the action of sodium on *o*-bromobenzyl bromide, through the dihydro-compound. Anthracene is also formed.

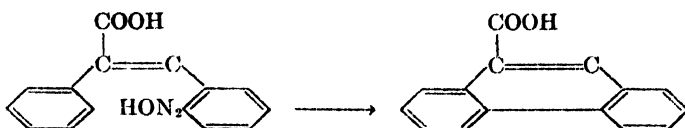


(3) By heating coumarone with benzene (*Kraemer*, *Ber.* **23**, 85):



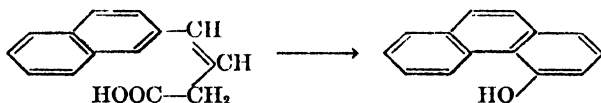
Chrysene is formed in a similar way from coumarone and naphthalene, and 1-naphthylamine from furan and aniline (p. 615).

(4) The diazonium compound of *o*-amino- $\alpha$ -phenylcinnamic acid gives phenanthrene carboxylic acids when treated with copper powder (*Pschorr*, Ber. 29, 496):

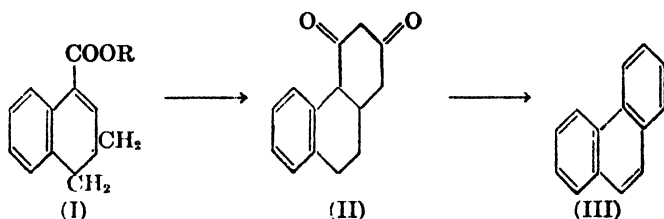


The reaction recalls the formation of diphenyl from benzene and phenyldiazonium chloride (p. 493), and that of fluorenone from the diazonium compound of *o*-aminobenzophenone (p. 681). Numerous phenanthrene derivatives can be prepared by generalising this synthesis. The method is suitable for preparing phenanthrene derivatives with substituents in known positions (*Pschorr*, Ber. 33, 162, 1810; 34, 3998; 39, 3106; *Mayer*, Ann. 403, 178).

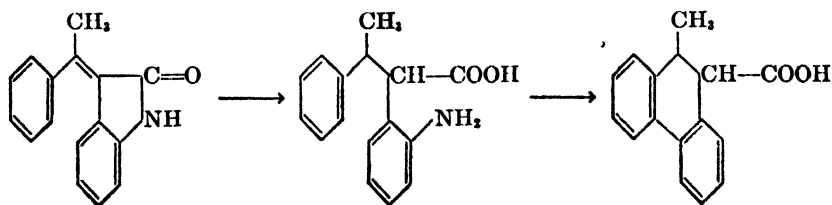
(5) The synthesis of 1-naphthol from styryl-acetic acid (phenylisocrotonic acid) can be applied to the formation of 4-hydroxyphenanthrene by heating 2-naphthylisocrotonic acid (*Ludwig*, Ann. 379, 351; *Klinkhardt*, Ann. 379, 362):



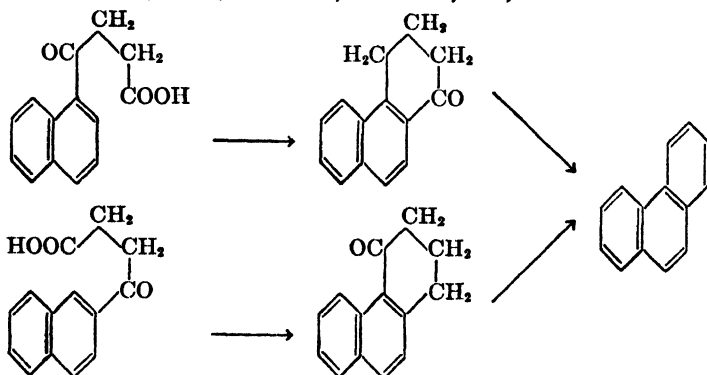
(6) The following synthesis of phenanthrene from a naphthalene derivative is interesting: 3,4-dihydro-1-naphthoic ester (I) condense with acetoacetic ester to give a diketo-octahydrophenanthrene carboxylic ester, which, on hydrolysis and loss of carbon dioxide, gives octahydro-diketophenanthrene (II); when this is distilled with zinc dust, phenanthrene is formed (III) (*Rabe*, Ber. 31, 1896):



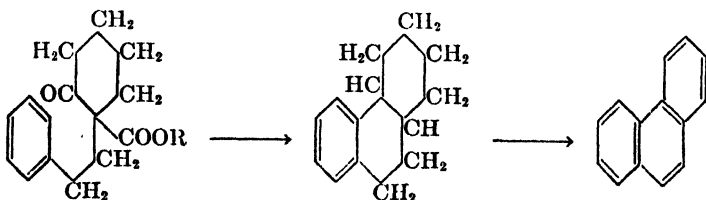
(7) A synthesis of 9-alkylated phenanthrenes, which cannot be obtained by *Pschorr*'s synthesis (4, above), consists of the condensation of acetophenone with oxindol. The condensation product is hydrogenated, decomposed to the amino-acid, and by diazotisation and boiling with copper powder, ring closure is effected, and 9-methyl-dihydrophenanthrene carboxylic acid is formed (*Windaus*, Ber. 57, 1875):



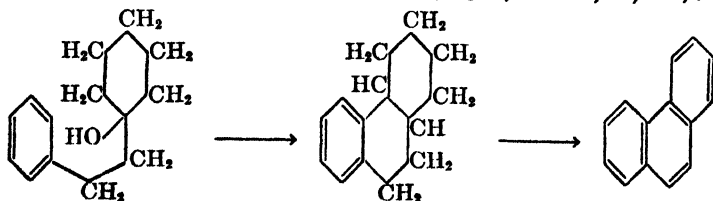
(8) The following synthesis is capable of general application. Naphthalene is condensed with succinic anhydride in nitrobenzene solution in the presence of aluminium chloride. The  $\beta$ -naphthoyl-1- and  $\beta$ -naphthoyl-2-propionic acids are reduced by Clemmensen's method, and the ring closed by treatment with 85% sulphuric acid, or with stannic chloride, when 1- and 4-keto-1,2,3,4-tetrahydrophenanthrene are formed. After separation of the keto-group the hydrophenanthrenes obtained are dehydrogenated with selenium, when phenanthrene is formed. The importance of this synthesis lies in the use of substituted naphthalenes and succinic anhydrides (*Haworth, J. 1932, 1125, 1784, 2248; Ruzicka, Helv. 15, 907*):



(9) Phenylethyl bromide reacts with the potassium salt of cyclohexanone carboxylic ester. The keto-ester produced is hydrolysed, decarboxylated, reduced to the alcohol, and the ring closed to octahydrophenanthrene by means of phosphorus pentoxide. Phenanthrene is obtained from the hydro-compound by dehydrogenation with selenium (*Bardhan, Sen Gupta, J. 1932, 2520; Haworth, ibid., 2720*):

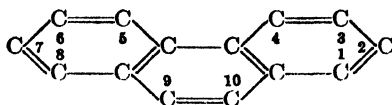


(10) Another method consists in condensing cyclohexanone with phenylethyl-magnesium bromide, giving 1-phenylethyl-cyclohexanol-1, and from this the same octahydrophenanthrene is obtained as in (9) (*Bogert, Science, 77, 289*):

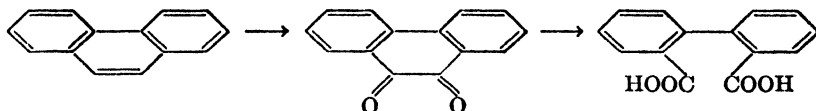


(11) Polyhydroxy-dibenzyls can be converted into hydroxy-dihydrophenanthrenes by oxygen and other mild oxidising agents (*Erdtmann*, Ann. 505, 195).

These methods of formation indicate that phenanthrene must be regarded as a diphenyl derivative, in which the two benzene rings are linked by  $\text{CH}=\text{CH}$  in two ortho-positions. With the four carbon atoms, the two benzene rings give rise to a third normal benzene ring:



In agreement with this formula, phenanthrene does not react with maleic anhydride, and its optical properties are those of a substance with three condensed benzene rings. The oxidation of phenanthrene, which leads first to phenanthraquinone then to diphenic acid, and *o*-phthalic acid, also supports this conclusion:



Phenanthrene and its derivatives are degradation products of many important naturally occurring substances, which contain the phenanthrene skeleton in a varying degree of hydrogenation. Thus, the alkaloids morphine, codeine, thebaine, colchicine and laurotetanine are phenanthrene derivatives. Many of the higher terpenes and resin acids, such as abietic acid; the sterols and bile acids, strophanthidine, the follicular hormone, the lichen dye telephoric acid, and the colouring matter of green decaying wood, xylindein all contain phenanthrene skeleton. In some cases the homologues of phenanthrene obtained from these natural substances—usually by dehydrogenation with zinc dust or selenium—are still of unknown constitution.

**Phenanthrene**  $\text{C}_{14}\text{H}_{10}$ , m.p.  $101^\circ$ , b.p.  $332^\circ$ , forms colourless crystals, which dissolve readily in ether and benzene, but more difficultly in alcohol and water. The solutions show a blue fluorescence. For the spectrochemistry of phenanthrene, see *Auwers*, Ann. 430, 230; 443, 181.

Picrate,  $\text{C}_{14}\text{H}_{10} \cdot \text{C}_6\text{H}_3(\text{OH})(\text{NO}_2)_3$ , yellow needles, m.p.  $144^\circ$ . For the preparation of phenanthrene from crude anthracene, see *Anschütz*, Ann. 196, 34; *Wense*, Ber., 19, 761.

#### ALKYLATED PHENANTHRENES:

|                       |                                                                 |                                                 |
|-----------------------|-----------------------------------------------------------------|-------------------------------------------------|
| 1-Methyl-phenanthrene | m.p. $118^\circ$                                                | } method (8) ( <i>Haworth</i> , J. 1932, 1125). |
| 2- " "                | m.p. $56^\circ$                                                 |                                                 |
| 3- " "                | m.p. $63^\circ$                                                 |                                                 |
| 4- " "                | m.p. $50^\circ$                                                 |                                                 |
| 9- " "                | m.p. $91^\circ$ ; method (7) ( <i>Windaus</i> , Ber. 57, 1871). |                                                 |

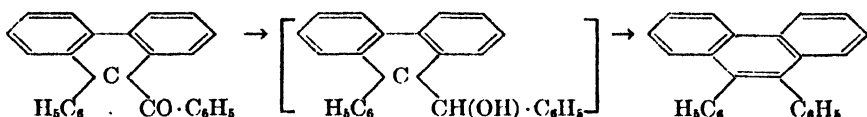
4-Methyl-phenanthrene has also been obtained by the dehydrogenation of podocarpic acid (*Radcliffe*, J. 1931, 2293), and 9-methyl-phenanthrene by the degradation of colchicine (*Windaus*, Nachr. Ges. Wiss. Göttingen, 1923, 17; C. 1923, III, 674).

It is to be noted that the syntheses of 3,5- and 4,5-dimethyl-phenanthrene are unsuccessful because of a wandering of the methyl group during dehydrogenation with selenium from position 5 to 8 (*Haworth*, J. 1934, 454).



|                                         | M.p.      | Method      |                                                  |
|-----------------------------------------|-----------|-------------|--------------------------------------------------|
| 1,2-Dimethyl-phenanthrene...            | 143°      | (8)         | (Haworth, J. 1934, 454).                         |
| 1,3-                                  " | .... 76°  | (8)         | "                                  "             |
| 1,4-                                  " | .... 77°  | (9)         | (Bardhan, J. 1932, 2520).                        |
| 1,5-                                  " | .... 58°  | (8)         | (Haworth, loc. cit.).                            |
| 1,6-                                  " | .... 88°  | (9)         | "                                  "             |
| 1,7-                                  " | .... 86°  | (9)         | (Bardhan, loc. cit.).                            |
| 1,8-                                  " | .... 192° | (8)         | } (Haworth, loc. cit.)                           |
| 1,9-                                  " | .... 88°  | (8)         |                                                  |
| 2,3-                                  " | .... 66°  | (8)         |                                                  |
| 2,4-                                  " | .... 111° | (8)         |                                                  |
| 2,5-                                  " | .... 47°  | (8)         |                                                  |
| 2,6-                                  " | .... 34°  | (8)         |                                                  |
| 2,7-                                  " | .... 102° | (8)         |                                                  |
| 2,9-                                  " | .... 57°  | (8)         |                                                  |
| 3,4-                                  " | .... 63°  | (8)         |                                                  |
| 3,6-                                  " | .... 141° | (9)         |                                                  |
| 9,10-                                "  | .... 139° | (See below) | (Pschorr, Ber. 39, 3110; Zincke, Ann. 362, 250). |

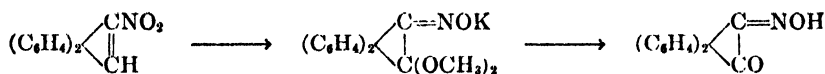
The following have been obtained: 1,2-Dimethylphenanthrene by dehydrogenation of the follicular hormone dicarboxylic acid, and aetiobilanic acid (*Bulenandt*, Ber. 66, 601); 1,7-dimethylphenanthrene, pimanthrene, by dehydrogenation of the resin acid from manila. 9,10-Dimethylphenanthrene by reduction of 9,10-dimethyl-9,10-dihydroxydihydrophenanthrene (p. 675) with hydriodic acid and phosphorus (*Pschorr*, Ber. 39, 3110; *Zincke*, Ann. 362, 250). For trimethylphenanthrenes see *Ruzicka*, Helv. 13, 1402; 14, 233; *Haworth*, J. 1932, 2248. 9,10-Diphenylphenanthrene,  $C_{14}H_{10}(C_6H_5)_2$ , m.p. 235°, is obtained synthetically by the action of aluminium chloride on tetraphenylethylene (p. 574) (*Biltz*, Ber. 38, 203). It is also formed by a remarkable atomic migration by the reduction of benzoyl-phenyl-fluorene (p. 680) with hydriodic acid and phosphorus, a reaction which corresponds to the formation of tetraphenyl-ethylene from  $\beta$ -benzopinacoline (*Werner*, Ber. 37, 2887):



**HALOGENO-PHENANTHRENES.** When chlorine acts on phenanthrene substitution products are formed. 9,10-Dichloro-, and 2,9,10-trichloro-phenanthrenes,  $C_{14}H_8Cl_2$  and  $C_{14}H_7Cl_3$ , m.p. 161° and 145° (*Schmidt*, Ber. 39, 3891). The latter is also obtained readily from 9,10-phenanthraquinone and phosphorus pentachloride (*Schmidt*, Ber. 44, 3248). Octachlorophenanthrene,  $C_{14}H_2Cl_8$ , m.p. 270–280°, splits up on further chlorination into  $C_6Cl_6$  and  $CCl_4$ . 9-Chlorophenanthrene, m.p. 49–53°, is produced by splitting off HCl from 9,10-phenanthrene dichloride (*Landqvist*, Ann. 417, 30). 3-Chlorophenanthrene, m.p. 81°, and 3,10-dichlorophenanthrene, m.p. 116°, see *Landqvist*, Ann. 369, 116; *Nylen*, Ber. 53, 163. Phenanthrene adds on bromine in carbon disulphide forming phenanthrene dibromide, which splits off HBr, forming 9-bromophenanthrene, m.p. 63°. This compound is oxidised by chromic acid to phenanthraquinone, and on further bromination gives 4,9-(4,10-)dibromophenanthrene, m.p. 113°. When the latter compound is oxidised it gives 4-bromophenanthraquinone (*Werner*, Ann. 321, 330; *Schmidt*, Ber. 37, 3553). For other dibromophenanthrenes, see *Landqvist*, Ber. 48, 1146; *Henstock*, J. 123, 3097.

**NITROPHENANTHRENES.** Three nitrophenanthrenes are formed by nitration of phenanthrene. One has been shown to be 3-nitrophenanthrene, m.p. 171° (*Schmidt*, Ber. 34, 3532). If nitration is carried out with a mixture of acetic anhydride and nitric acid in glacial acetic acid, 9-nitrophenanthrene, m.p. 117°, is formed. The same compound is formed by the action of oxides of nitrogen on phenanthrene and treatment of the product with sodium ethylate solution (*Schmidt*, Ber. 36, 2508). When 9-nitrophenanthrene is boiled with methyl

alcoholic potash, 2 mols. of potassium methylate are added, and phenanthraquinone oxime dimethyl-acetal is first formed, which changes to the isomeric phenanthraquinone monoxime



(Meisenheimer, Ann. 355, 307). Cf. also the analogous conversion of 7-nitrostilbene (p. 560), 1- and 2-nitronaphthalene (p. 614), and 9-nitroanthracene (p. 650).

**AMINOPHENANTHRENES** or **PHENANTHRYLAMINES** can be obtained by reduction of the nitrophenanthrenes, and from the phenanthrols by heating with ammonium salts. 2-Aminophenanthrene,  $\text{C}_{14}\text{H}_9\text{NH}_2$ , m.p.  $85^\circ$ ; 3-aminophenanthrene, m.p.  $87^\circ$ ; 9-aminophenanthrene, m.p.  $136^\circ$ , has also been prepared from the azide of 9-phenanthrene carboxylic acid (Werner, Ann. 321, 312; Schmidt, Ber. 34, 1461; Pschorr, Ber. 35, 2726). 9,10-Diaminophenanthrene,  $\text{C}_{14}\text{H}_8(\text{NH}_2)_2$ , obtained by reduction of phenanthraquinone dioxide, gives diphenanthrylazine,  $\text{C}_{14}\text{H}_8\text{N}_2\text{C}_{14}\text{H}_8$ , on oxidation in the air (Pschorr, Ber. 35, 2738).

**PHENANTHRENE SULPHONIC ACIDS.** When phenanthrene is sulphonated, four isomeric acids are obtained: 1-, 2-, 3-, and 9-phenanthrene sulphonic acids (1-methyl ester, m.p.  $102^\circ$ ; 2-sulphonyl chloride, m.p.  $156^\circ$ ; 3-sulphonyl chloride, m.p.  $108^\circ$ ; 9-sulphonyl chloride, m.p.  $125^\circ$ ) (Werner, Ann. 321, 248; Landqvist, Ann. 392, 76; Fieser, Am. 51, 2460). For disulphonic acids, see Fieser, loc. cit.

**HYDROXYPHENANTHRENES**, or **PHENANTHROLS**, are obtained from the sulphonic acids or aminophenanthrenes by fusion with potash. Their ethers can also be obtained from synthetic phenanthrene-9-carboxylic acid, by splitting off carbon dioxide. In this way the constitution of the five possible, and known, isomerides has been obtained:

|               |                    |              |                                           |
|---------------|--------------------|--------------|-------------------------------------------|
| 1-Phenanthrol | m.p. $156^\circ$ ; | methyl ether | m.p. $106^\circ$ (Fieser, Am. 51, 2460).  |
| 2- "          | m.p. $168^\circ$ ; | " "          | m.p. $99^\circ$ (Werner, Ann. 321, 76).   |
| 3- "          | m.p. $124^\circ$ ; | " "          | m.p. $63^\circ$ (Werner, loc. cit.).      |
| 4- "          | m.p. $108^\circ$ ; | " "          | m.p. $68^\circ$ (Pschorr, Ber. 33, 1826). |
| 9- "          | m.p. $153^\circ$ ; | " "          | m.p. $97^\circ$ (Werner, loc. cit.).      |

1- and 4-Phenanthrol have also been obtained by heating the corresponding  $\alpha$ -naphthyl-paraconic acids (Shoosmith, J. 1928, 2332). 9-Phenanthrol ("phenanthrone") has been prepared by reducing phenanthraquinone with hydriodic acid, and from phenanthraquinone dichloride,  $\text{C}_{14}\text{H}_8\text{OCl}_2$ . With phenyldiazonium salts it gives *o*-benzene-azo-9-phenanthrol, m.p.  $165^\circ$ , which is identical with the reaction product of phenylhydrazine on phenanthraquinone (p. 675). 2-, 3-, and 9-Phenanthrols resemble 2-naphthol (Werner, Ann. 321, 276; Schmidt, Ber. 34, 1461). 1,2-Dimethylphenanthrol-7, m.p.  $198^\circ$ , methyl ether, m.p.  $156^\circ$ , has been obtained by dehydrogenation of follicular hormone dicarboxylic acid (Ber. 66, 601), and synthetically (Haworth, J. 1934, 864). 3-Phenanthrene-thiol,  $\text{C}_{14}\text{H}_9\text{S}$ , m.p.  $113^\circ$ , is the reduction product of phenanthrene-sulphonyl chloride with zinc dust (Field, J. 107, 1214).

Of the aminophenanthrols (Ann. 312, 286, 295) and the dihydroxyphenanthrenes, the 9,10-compounds are the most important. 9,10-Aminohydroxyphenanthrene,  $\text{C}_{12}\text{H}_7 \begin{array}{c} \diagup \text{COH} \\ \diagdown \text{CNH}_2 \end{array}$ , obtained by reduction of phenanthraquinone ox-

ime, -imine, or phenylhydrazone. It readily passes into phenanthrene-hydroquinone, 9,10-dihydroxyphenanthrene,  $\text{C}_{14}\text{H}_8(\text{OH})_2$ , m.p.  $148^\circ$ . This is best prepared by reduction of phenanthraquinone with zinc and glacial acetic acid, or with hydrogen sulphide in alcoholic solution, and readily passes again into phenanthraquinone. Nitrophenanthrene-hydroquinones have been obtained in a similar way (Schmidt, Ber. 35, 3117). For radicals with monovalent oxygen, derived from 9,10-phenanthrene-hydroquinone, see Goldschmidt, Ann. 438, 202, and the section on free radicals, Vol. IV.

| Dihydroxyphenanthrene |      | Compound       | M.p. | Reference                                           |
|-----------------------|------|----------------|------|-----------------------------------------------------|
| Compound              | M.p. |                |      |                                                     |
| 1,2-                  | 178° | Dimethyl ether | 102° | <i>Fieser</i> , Am. 51, 1896.                       |
| 1,6-                  | 253° | Dimethyl ether | 117° | <i>Fieser</i> , Bull. Inst. Pin. 1929, sp. no. 108. |
| 1,7-                  | 205° | Diacetate      | 125° | <i>Fieser</i> , Bull. Inst. Pin. 1929, sp. no. 108. |
| 2,3-                  | 159° | Dimethyl ether | 131° | <i>Mosettig</i> , Am. 52, 2988.                     |
| 2,6-                  | 239° | Dimethyl ether | 87°  | <i>Fieser</i> , loc. cit.                           |
| 2,7-                  | 265° | Dimethyl ether | 168° | <i>Fieser</i> , loc. cit.                           |
| 3,4-                  | 143° | Dimethyl ether | 44°  | <i>Fieser</i> , Am. 51, 940.                        |
| 3,6-                  | 225° | Dimethyl ether | 105° | <i>Fieser</i> , Bull. Inst. Pin. 1929, sp. no. 108. |
| 3,9-(10?)             | 175° | Dibenzoate     | 125° | <i>Schmidt</i> , Ber. 43, 433.                      |
| 9,10-                 | 148° | Diacetate      | 202° | <i>Schmidt</i> , Ber. 43, 790.                      |

3,4-Dihydroxyphenanthrene, morphol, m.p. 143°, is obtained from 3-phenanthrol-4-aldehyde by oxidation with alkaline hydrogen peroxide (*Barger*, J. 113, 218). 3,4-Dimethoxyphenanthrene, dimethylmorphol, is obtained from the 9-carboxylic acid (see above), and by methylation of the corresponding monomethyl ether, methylmorphol,  $C_{14}H_8(OH)(OCH_3)$ , which is a degradation product of the alkaloid codeine (*Pschorr*, Ber. 33, 1816). For trihydroxyphenanthrenes,  $C_{14}H_7(OH)_3$ , see *Bongerichten*, Ber. 39, 1718; *Fieser*, Am. 51, 1896.

**PHENANTHRENE CARBOXYLIC ACIDS:** The nitriles of these acids are obtained by distilling the salts of the sulphonic acids with potassium ferrocyanide:

- 1-Cyanophenanthrene m.p. 128° (*Fieser*, Am. 54, 4110).
- 2- " m.p. 105° (*Werner*, Ann. 321, 322).
- 3- " m.p. 102° (*Werner*, loc. cit.)
- 9- " m.p. 104° (*Werner*, loc. cit.; *Mosettig*, Am. 54, 3328).

The carboxylic acids are obtained from the nitriles, but 9-phenanthrene-carboxylic acid and its substitution products are also obtained synthetically by method 4 (p. 669).

- 1-Phenanthrene carboxylic acid m.p. 233° (*Fieser*, Am. 54, 4110).

- 2- " " " m.p. 258°
  - 3- " " " m.p. 269°
  - 9- " " " m.p. 250°
- (*Werner*, Ann. 321, 322; *Mosettig*, Am. 52, 3704)

1-, 2-, 3-, and 4-Methoxyphenanthrene-9-carboxylic acids,  $C_{14}H_8(OCH_3)COOH$ , m.p. 215°, 228°, 239°, and 224°, respectively, and 3,4-dimethoxyphenanthrene-9-carboxylic acid,  $C_{14}H_7(OCH_3)_2COOH$ , m.p. 228°, are obtained from the corresponding methoxyamino- $\alpha$ -phenyl-cinnamic acids. They lose carbon dioxide on distillation forming the methoxy-phenanthrenes (*Pschorr*, Ber. 34, 3998). A remarkable transformation occurs on heating 5- and 7-methylphenanthrene-9-carboxylic acid. They give phenyl-methyl-coumarins (*Stoermer*, Ann. 409, 25). No carbon dioxide is split off when 2- and 3-methylphenanthrene-9-carboxylic acids are heated (*Mayer*, Ann. 403, 178).

Phenanthrene-3-carboxylic acid is produced with a little -2- and -9-carboxylic acid by the action of oxalyl chloride and aluminium chloride on phenanthrene (*Mosettig*, Am. 54, 3328). 2,3- and 3,2-Phenanthrol-carboxylic acids,  $C_{14}H_8(OH)COOH$ , m.p. 227° (decomp.) and 303° (decomp.), respectively, are obtained by the salicylic acid synthesis from 2- and 3-sodio-phenanthrols by heating with carbon dioxide under pressure. They are yellow, and resemble 2,3-naphthol-carboxylic acid (p. 636) (*Werner*, Ber. 35, 4419). 3,4-Dimethoxyphenanthrene-8-carboxylic acid, m.p. 196°, has been obtained from apomorphin, a transformation product of morphine, by methylation and degradation (*Pschorr*, Ber. 40, 1998).

**PHENANTHRENE ALDEHYDES** have been prepared by the catalytic reduction of the acid chlorides. Phenanthrene-2-aldehyde, m.p. 59° (*Mosettig*, Am. 55, 2995); -3-aldehyde, m.p. 80°, -9-aldehyde, m.p. 101°. For hydroxyaldehydes of phenanthrene, see *Mosettig*, Am. 55, 2981.

**HYDROPHENANTHRENES** are obtained by reduction of phenanthrene with

sodium and amyl alcohol, or hydrogen in the presence of finely divided nickel, or colloidal platinum or palladium, or by heating with hydrogen iodide and phosphorus: 9,10-(*meso*-)dihydrophenanthrene, m.p. 35° (Schroeter, Ber. 62, 645). 1,2,3,4-Tetrahydrophenanthrene, tetranthrene, C<sub>14</sub>H<sub>14</sub>, m.p. 33–34°, picrate, m.p. 111° (Schroeter, Ber. 62, 651). 1-Keto- and 4-ketotetranthrene, m.p. 96° and 69°, respectively (Bardhan, J. 1932, 2520; Schroeter, Ber. 62, 651), are obtained synthetically by method (8). 1,2,3,4,5,6,7,8-Octahydrophenanthrene, octanthrene, m.p. 16.7°, b.p. 168–172° (14 mm.). 1-Keto-octanthrene, m.p. 81–82° (Schroeter, Ber. 57, 2028). 1,2,3,4,9,10,11,12-Octahydrophenanthrene, b.p. 135° (9 mm.), is obtained synthetically by methods (9) and (10). 1,3-Diketo-compound, m.p. 160°, obtained by method (6) (Rabe, Ber. 31, 1896). The individuality of hexa-, deca-, dodeca-, and perhydro-phenanthrene, C<sub>14</sub>H<sub>14</sub>, C<sub>14</sub>H<sub>20</sub>, C<sub>14</sub>H<sub>22</sub>, and C<sub>14</sub>H<sub>24</sub>, b.p. 289–290°, 274–275°, 268°, and 266–276°, respectively, is uncertain (Ipatiev, Ber. 41, 1000; Schmidt, Ber. 41, 4225; Breteau, C.r. 140, 942; 151, 1368; Schroeter, Ber. 57, 2025).

Derivatives of 9,10-dihydrophenanthrene are obtained by the action of alkyl- and aryl-magnesium halides on phenanthraquinone. 9,10-Dimethyl-, -diethyl-,

and -diphenyl-9,10-dihydroxy-dihydrophenanthrenes, (C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> $\begin{matrix} \diagup C(OH)R \\ \diagdown C(OH)R \end{matrix}$ , m.p.

164°, 122°, and 179°, respectively. They are reduced by hydriodic acid and phosphorus to 9,10-dialkyl-phenanthrenes (p. 672), and are oxidised by chromic

acid to *o,o'*-diacyl-diphenylenes, (C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> $\begin{matrix} \diagup COR \\ \diagdown COR \end{matrix}$ . The original glycols and their

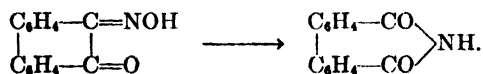
stereoisomeric forms are regained by reduction. Heating with dehydrating agents results in a pinacol transformation, giving 10,10-dialkyl-phenanthrones,

(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> $\begin{matrix} \diagup C=O \\ \diagdown CR_2 \end{matrix}$ . 10,10-Dimethyl-, -diethyl-, and -diphenylphenanthrone, m.p.

75°, 65°, and 198° (Zincke, Ann. 362, 242; Werner, Ber. 37, 2887; Acree, Amer. Chem. J. 33, 180).

9,10-Phenanthraquinone, (C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(CO)<sub>2</sub>, m.p. 208°, is an orange-yellow substance, forming needle-shaped crystals, which distil unchanged. It is obtained by the action of chromic acid on phenanthrene in glacial acetic acid, or heating with chromic acid mixture. It dissolves readily in hot alcohol, ether, and benzene, and slightly in water. Its dark green solution in concentrated sulphuric acid precipitates phenanthraquinone again on addition of water. If benzene containing thiophene, and sulphuric acid are added to a solution of phenanthraquinone in glacial acetic acid, a bluish-green colour is formed. In its reactions, phenanthraquinone resembles 1,2-naphthaquinone closely. It has no odour, is not volatile in steam, combines with one or two molecules of hydroxylamine, and with hydrocyanic acid, and is reduced by sulphurous acid. Comparison of the dyeing properties of phenanthraquinone derivatives with the corresponding anthraquinone derivatives shows that dyes obtained from the former are better and faster (Brass, Z. angew. Chem. 37, 67).

Phenanthraquinone-monoxime, C<sub>14</sub>H<sub>8</sub>O(NOH), golden-yellow needles, m.p. 158°, isomerises on heating with glacial acetic acid and hydrochloric acid to 130°, with formation of diphenimide (p. 506) (Wigerhoff, Ber. 21, 2356).



The dioxime forms an anhydride, C<sub>14</sub>H<sub>8</sub> $\begin{matrix} \diagup N \\ \diagdown N \end{matrix}$ O, m.p. 181°, a furazane derivative. The monophenylhydrazone of phenanthraquinone is identical with 9,10-benzene-azo-phenanthrol (C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> $\begin{matrix} \diagup C\cdot OH \\ \diagdown C=N:NC_6H_5 \end{matrix}$  (p. 673). The acyl-phenylhydrazones, obtained by the action of *as*-acetyl- and -benzoyl-phenyl-hydrazine

with phenanthraquinones, pass spontaneously into the isomeric O-acyl-compounds of 9,10-benzene-azo-phenanthrol with a migration of the acyl radical (*Auwers*, *Ann.* 378, 211) (*cf.* the analogous behaviour of 1,2-naphthaquinones, p. 631).

Phenanthraquinone, being an *o*-diketone, reacts with *o*-diamines giving phenazine derivatives, and with *o*-aminophenol to give phenoxazines. For its condensation with acetoacetic ester, and acetone, see *Japp*, *J.* 61, 1; *Wadsworth*, *J.* 61, 105. Phenanthraquinone is oxidised to diphenic acid by chromic acid mixture, or boiling with alcoholic potash. When heated with soda-lime diphenylene-ketone (p. 681), fluorene (p. 678), and diphenyl are formed. When boiled with aqueous caustic soda, diphenylene-glycolic acid (p. 682), fluorene-alcohol, (p. 680), and diphenylene-ketone are formed, and when distilled with zinc dust, phenanthrene is obtained.

It is reduced by sulphurous acid, or hydrogen sulphide to phenanthrene-hydroquinone (p. 673), and by hydriodic acid and phosphorus to phenanthrene (p. 673). With hydriodic acid and phosphorus in glacial acetic acid, phenanthrene-hydroquinone monoacetate, m.p. 78°, is formed (*Japp*, *J.* 63, 774; 71, 1115). Mixtures of phenanthraquinone and aldehydes give acydl-phenanthrene-hydroquinone in sunlight (*Klinger*, *Ann.* 249, 137). It can condense with phenols to give phenoxyphenanthrene-hydroquinones (*Ger. Pat.* 109,344).

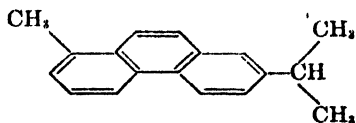
Bromine adds on to phenanthraquinone at low temperatures, forming  $C_{14}H_8O_2Br_2$  (*Schmidt*, *Ber.* 37, 3556). At 100°, substitution products are obtained: 2-, and 3-bromo- and 2,7-dibromophenanthraquinone, m.p. 234°, 269°, and 323°; 3- and 4-bromophenanthraquinone, m.p. 269° and 126°, are obtained by oxidation of 3,9- and 4,9-dibromophenanthrene, with chromic acid, and 2-chlorophenanthraquinone, m.p. 253°, is obtained similarly from 2,9,10-trichlorophenanthrene (*Schmidt*, *Ber.* 39, 3893; 43, 430; 44, 3421).

When phenanthraquinone is heated with nitric acid, 2- and 4-nitrophenanthraquinone,  $C_{14}H_7(NO_2)_2O_2$ , m.p. 260° and 177°, respectively, are obtained if the action is short. If it is more energetic, 2,7- and 4,5-dinitrophenanthraquinone,  $C_{14}H_5(NO_2)_4O_2$ , m.p. 300–303° and 228°, respectively, are obtained. 3-Nitrophenanthraquinone, m.p. 275°, is obtained from 9-bromophenanthrene (p. 672), and from 9,10-diacetaminophenanthrene with nitric acid (*Schmidt*, *Ber.* 41, 3679). Oxidation of the nitrophenanthraquinones with chromic acid mixture gives nitrodiphenic acids (p. 506). Aminophenanthraquinones are formed by reduction and from these hydroxy-phenanthraquinones can be obtained (*Schmidt*, *Ber.* 36, 3726; *Brass*, *Ber.* 55, 541). These hydroxy-compounds can also be obtained by oxidation of the acylated phenanthrols with chromic acid. 1-Hydroxy-phenanthraquinone,  $C_{14}H_7(OH)O_2$ , m.p. 227°, is obtained from *o*-methoxybenzil by treatment with aluminium chloride (*Ber.* 63, 2613; *Fieser*, *Am.* 51, 2460). 2-Hydroxyphenanthraquinone, m.p. 283°, violet-black needles. 3-Hydroxyphenanthraquinone, needles similar to alizarin, m.p. 330° (decomp.), sublimes. 4-Hydroxyphenanthraquinone, a red powder, m.p. 285° (*Schmidt*, *Ber.* 44, 740). 3,4-Dihydroxyphenanthraquinone, morpholquinone,  $C_{14}H_6(OH)_2O_2$ , (diacetate, m.p. 196°), is obtained from 3-hydroxyphenanthraquinone, through the nitro- and amino-compounds (*Schmidt*, *Ber.* 41, 3696). For further dihydroxyphenanthraquinones see *Schmidt*, *Ber.* 56, 1331; *Brass*, *Ber.* 57, 128; *Fieser*, *Bull. Inst. Pin.* 1929, sp. no. 108.

1- and 3-Phenanthraquinone sulphonic acids,  $C_{14}H_7O_2SO_3H$ , are obtained from the corresponding phenanthrene sulphonic acids by oxidation with chromic acid (*Werner*, *Ann.* 321, 339; *Fieser*, *Am.* 51, 2460).

Besides 9,10-phenanthraquinone 1,2-, 1,4-, and 3,4-phenanthraquinones, m.p. 222°, 155°, and 133° respectively, are also known. They are obtained by oxidation of the corresponding aminophenanthrols with chromic acid (*Fieser*, *Am.* 51, 940, 1896, 2460). 1,4,9,10-Phenanthrene-diquinone is obtained by oxidation of 1,4-phenanthraquinone with lead tetracetate. It is very unstable (*Brass*, *Ber.* 57, 133). The lichen dye telephoric acid, is a derivative of 1,4,7-trihydroxy-9,10-phenanthraquinone-6-carboxylic acid, with a side-chain in the 2-position.

Retene, or 1-methyl-7-isopropyl-phenanthrene,  $CH_3 \cdot C_{14}H_8 \cdot C_3H_7$ , m.p. 98°, b.p. 394°, is a homologue of phenanthrene. It is found in pine tar, and in some natural resins, and is separated from their highest boiling fractions. It is produced by distillation of abietic acid (which is to be regarded as decahydroretene carboxylic acid; *Ruzicka*, *Helv.* 15, 1289) with sulphur (*Vesterberg*, *Ber.* 36, 4200; *Fieser*, *Bull. Inst. Pin.* 1929, sp. no. 108). Picrate, m.p. 127°.

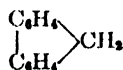


For the synthesis of retene, see *Haworth*, J. 1932, 1784; *Bardhan*, J. 1932, 2798. When oxidised with chromic acid in glacial acetic acid it gives **retene-quinone**,  $C_{18}H_{10}O_2$ , m.p.  $197^\circ$ , which is completely analogous in its properties to phenanthraquinone. With caustic soda it forms **retene-diphenic acid**,  $C_{18}H_{10}(COOH)_2$ , and **retene-glycolic acid**,  $C_{18}H_{10}C(OH) \cdot COOH$ . Oxidation with permanganate gives **retene-ketone**,  $CH_3[1]C_6H_4 \begin{array}{c} \diagup \diagdown \\ \text{CO} \end{array} C_6H_4[7]C_6H_7$ , 7-hydroxy-isopropyl-di-

**phenylene-ketone-1-carboxylic acid**, and **diphenylene-ketone-1,7-dicarboxylic acid**. The latter is further converted into a mixture of 1,2,3- and 1,2,4-benzenetricarboxylic acids. 7-Hydroxy-isopropyl-diphenylene-ketone-1-carboxylic acid can be broken down to *p*-isopropylidiphenyl, by treatment with caustic potash, reduction with hydriodic acid, and removal of the carboxyl group. In this way, the positions of the side-chains in retene can be determined (*Bucher*, Am. 32, 374). By the action of oxalyl chloride and aluminium chloride on retene,  $\alpha$ -**retene-carboxylic acid** is formed. It can also be obtained by oxidation of acetyl-retene (*Bogert*, Proc. Nat. Acad. Sci. 18, 417). For monosubstitution products of retene, see *Komppa*, Am. 52, 5009; *Fieser*, Am. 53, 4120. Derivatives of dihydrotene, see *Komppa*, Am. 54, 2900. When retene is heated with hydriodic acid and phosphorus to  $250^\circ$ , **dodecahydrotene**, "dehydrofichtelite,"  $C_{18}H_{20}$ , an oil, b.p.  $336^\circ$ , is formed (*Hell*, Ber. 22, 498; *Bamberger*, Ber. 22, 635; *Liebermann*, Ber. 22, 780; *Spiegel*, Ber. 22, 3369).

## 5. FLUORENE GROUP

Fluorene is related to phenanthrene. Just as phenanthrene may be regarded as a *sym-o,o'*-ethylene derivative of diphenyl, fluorene can be regarded as the *o,o'*-methylene derivative of it, and may also be regarded as diphenylenemethane. On the other hand, like indene, it can be regarded as a condensed cyclopentadiene derivative. Fluorene also bears some relationship to diphenylene sulphide, diphenylene oxide, and diphenylene imide or carbazol, the dibenzo-derivative of thiophene, furan, and pyrrole:



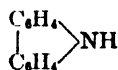
Fluorene



Diphenylene  
oxide

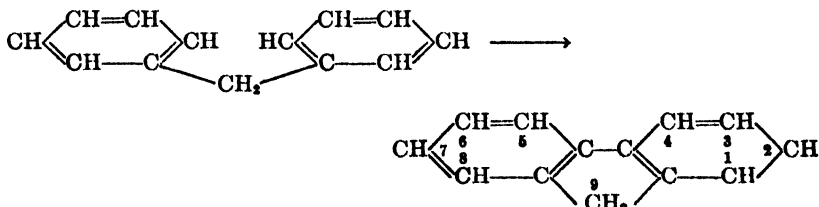


Diphenylene  
sulphide



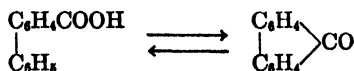
Diphenylene  
imide

*General methods of formation:* 1. By passing the vapour of diphenylmethane through a red-hot tube:

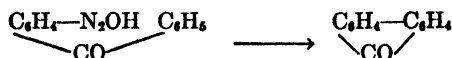


2. When diphenyl-*o*-carboxylic acid or its salts are heated, fluorenone is

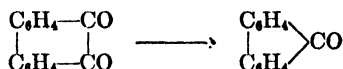
formed, and this can easily be reduced to fluorene. Conversely, if fluorenone is fused with alkali the acid is formed:



3. The diazonium compound of *o*-amino-benzophenone gives fluorenone, with evolution of nitrogen (Graëbe, Ber. 29, 836; Ullmann, Ber. 31, 1694; cf. method 4 under phenanthrene, p. 669):



4. Phenanthraquinone (p. 676) gives fluorenone when treated with oxidising agents:



Fluorene,  $\text{C}_{13}\text{H}_{10}$ , diphenylene-methane, m.p.  $113^\circ$ , b.p.  $295^\circ$  (picrate, m.p.  $81^\circ$ ), forms colourless needles with a blue fluorescence. It is found in coal-tar (in the fraction boiling at  $270\text{--}300^\circ$ ). It forms a sodium salt  $(\text{C}_6\text{H}_4)_2\text{CHNa}$  on heating with sodium, or better with sodamide to  $120\text{--}150^\circ$ . By means of this compound it can be separated from other hydrocarbons in coal-tar (Weissgerber, Ber. 41, 2913). Fluorene is obtained by pyrolysis of diphenylmethane. It can also be prepared by reduction of fluorenone with zinc dust or hydriodic acid and phosphorus at  $160^\circ$ . It is oxidised by chromic acid back to fluorenone. The hydrogen atoms of the  $\text{CH}_2$  group in fluorene are, to some extent, mobile, as they are in cyclopentadiene and indene. When heated with caustic potash and benzyl chloride, dibenzyl-fluorene,  $(\text{C}_6\text{H}_5)_2\text{C}(\text{CH}_2\text{C}_6\text{H}_5)_2$ , m.p.  $148^\circ$ , is formed. Fluorene condenses with benzaldehyde, cinnamaldehyde, etc., in the presence of sodium ethylate, forming benzylidene-fluorene,  $(\text{C}_6\text{H}_5)_2\text{C}:\text{CHC}_6\text{H}_5$ , m.p.  $76^\circ$ , and cinnamylidene-fluorene,  $(\text{C}_6\text{H}_5)_2\text{C}:\text{CH}\cdot\text{CH}:\text{CHC}_6\text{H}_5$ , m.p.  $154^\circ$ . Unlike the fulvenes these compounds are colourless or only slightly coloured. With acetaldehyde in pyridine it forms dehydro-ethylidene-bis-fluorene,  $(\text{C}_6\text{H}_4)_2\text{C}:\text{C}(\text{CH}_3)\cdot\text{CH}(\text{C}_6\text{H}_4)_2$ , in yellow crystals, which are unaffected by permanganate. If this compound is treated with zinc dust in glacial acetic acid, colourless ethylidene-bis-fluorene, m.p.  $262\text{--}263^\circ$ , is formed. This is converted again into the dehydro-compound by atmospheric oxygen (Pummerer, Ber. 46, 2386). Fluorene combines with ethyl oxalate forming fluorene oxalic ester,  $(\text{C}_6\text{H}_4)_2\text{CHCOCOO}\cdot\text{C}_2\text{H}_5$ , m.p.  $75^\circ$  and with ethyl formate to give formyl-fluorene or diphenylene-acetaldehyde,  $(\text{C}_6\text{H}_4)_2\text{CH}\cdot\text{CHO}$ , m.p. about  $70^\circ$  (Wislicenus, Ber. 43, 2719). With amyl nitrite and ethyl nitrate under the influence of alcohol-free potassium ethylate, fluorene gives fluorenone-oxime,  $(\text{C}_6\text{H}_4)_2\text{C}:\text{NOH}$ , and 9-nitrofluorene,  $(\text{C}_6\text{H}_4)_2\text{CHNO}_2$ , which, like phenylnitromethane (p. 256) exists in an acid, alkali-soluble *aci*-form, m.p.  $135^\circ$ , and a neutral form insoluble in alkali, m.p.  $182^\circ$  (Thiele, Ann. 347, 290; Ber. 33, 852; Wislicenus, Ber. 41, 3334). The power of fluorene to enter into condensations is increased by the introduction of halogen or nitro-groups (Sieglitz, Ber. 53, 1232; Loevenich, J. pr. [2], 116, 325).

Reduction of fluorene with hydriodic acid and phosphorus, or hydrogen and nickel, gives rise to perhydrofluorene,  $\text{C}_{13}\text{H}_{22}$ , b.p.  $256\text{--}258^\circ$ ,  $d_{20} 0.9203$  (Spiegel, Ber. 42, 920; Ipatiev, Ber. 42, 2093). It is interesting to note that a hexahydrofluorene,  $\text{C}_{13}\text{H}_{18}$ , can be obtained by extraction of coal with benzene, or distillation *in vacuo* (Pictet, Ber. 44, 2486). If 1-benzyl-cyclohexanol is heated with phosphorus pentoxide, a hexahydrofluorene,  $\text{C}_{13}\text{H}_{18}$ , b.p.  $137^\circ$  (15 mm.), is obtained which, however, cannot be converted into fluorene by dehydrogenation (Cook, J. 1933, 1098).

By bromination of fluorene in boiling chloroform, 2,7-dibromofluorene,  $\text{C}_{13}\text{H}_8\text{Br}_2$ , m.p.  $164^\circ$ , and 2,6(?)7-tribromofluorene,  $\text{C}_{13}\text{H}_7\text{Br}_3$ , m.p.  $200^\circ$ , are formed (Schmidt, Ber. 38, 3764). In the cold 2-bromofluorene, m.p.  $111.5^\circ$ , is produced (Courtot, Bull. [4], 41, 58).

On chlorination, fluorene gives 2-chlorofluorene and 2,7-dichlorofluorene (*Buffle*, *Helv.* 15, 1485). 2-Chlorofluorene, m.p. 98°, is obtained from the 2-amino-compound through the diazonium compound (*Courtot*, *Bull.* [4], 41, 58; *C.r.* 184, 1179). 9-Chlorofluorene,  $C_{13}H_9Cl$ , m.p. 90°, is obtained by the action of phosphorus pentachloride on fluorene alcohol (p. 680) (*Werner*, *Ber.* 37, 2896). 2,7,9,9-Tetrachlorofluorene is obtained by the action of phosphorus pentachloride on fluorene-2,7-disulphonic acid (*Courtot*, *C.r.* 178, 2259). 2-Iodofluorene, m.p. 128°, is obtained from 2-amino-fluorene (*Chanussot*, *Bull.* [4], 41, 1625; *Courtot*, *Ann. chim.* [10], 14, 5).

Nitration of fluorene in glacial acetic acid gives rise to 2-nitrofluorene,  $C_{13}H_9NO_2$ , m.p. 158°, which can be converted by the usual methods into 2-amino-, diazo-, and -hydroxy-fluorene, and 2-fluorenyl-hydrazine. By nitration of acetaminofluorene, 2,7- and 2,1-aminonitrofluorene, m.p. 232° and 206° (corr.), are obtained, which give 2,7- and 2,1-diaminofluorene, m.p. 164° and 193° (corr.) (*Diels*, *Ber.* 34, 1758; 35, 3284). 9-Aminofluorene, m.p. 62°, is obtained by the reduction of fluorenone-oxime, (*Schmidt*, *Ber.* 41, 1243; *Kuhn*, *Ber.* 58, 1436; *Kliegl*, *Ber.* 59, 634).

2,5- and 2,7-Dinitrofluorene, m.p. 207° and 334°, respectively, are obtained by nitration of 2-nitrofluorene. From these, 2,5- and 2,7-diaminofluorene, m.p. 175° and 165°, respectively, are obtained (*Morgan*, *J.* 1926, 2891; *Courtot*, *Ann. chim.* [10], 14, 5). 2,9-Dinitrofluorene, m.p. 136°, white crystals, is obtained by the action of nitric acid on 9-nitrofluorene or 9-fluorene oxalic ester (*Wieliczewus*, *Ann.* 436, 4). 4-Nitrofluorene, see *Courtot*, *loc. cit.* 3-Nitrofluorene, m.p. 105°, has been obtained through the 2-amino-3-nitro compound (*Bardout*, *An. soc. quim. Argentina* 19, 117; *C.* 1932, I, 941).

By the action of chlorosulphonic acid on fluorene, fluorene-2-sulphonic acid, m.p. 154-155°, is formed. With more energetic treatment, fluorene-2,7-disulphonic acid is obtained. This acid has also been obtained, together with two isomeric disulphonic acids, by sulphonation of fluorene with conc. sulphuric acid (*Schmidt*, *Ann.* 390, 217; *Courtot*, *C.r.* 178, 2259).

For nitro- and amino-fluorene sulphonic acids, see *Courtot*, *Ann. chim.* [10], 14, 5. For arsenic acids of the fluorene series, see *Morgan*, *J.* 1932, 1634. For free radicals, with fluorenyl groups, see Vol. IV.

Retene-fluorene, 1-methyl-7-isopropyl-diphenylene-methane,

$(CH_3)_2C_6H_3 \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} CH_2 \\ CH_2 \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} C_6H_5$ , m.p. 97°, is obtained from its ketone by distillation with zinc dust.

9-Phenyl-fluorene, phenyl-diphenylene-methane,  $(C_6H_5)_2CHC_6H_5$ , m.p. 146°, is obtained (1) from triphenylchloromethane,  $(C_6H_5)_3Cl$ , or potassium triphenyl methane (p. 525) by heating; (2) by distilling triphenylcarbinol with crystalline phosphoric acid (*Kliegl*, *Ber.* 38, 284); (3) from fluorene alcohol, benzene, and sulphuric acid (*Henriot*, *Bull.* [3], 1, 774); (4) from 9-chlorofluorene, benzene, and aluminium chloride; (5) from hydrofluoric acid (p. 544) by distillation with soda-lime, and (6) by reduction of 9-phenylfluorenol, phenyl-diphenylene carbinol,

$C_6H_5 \begin{array}{c} \diagup \\ \diagdown \end{array} C \begin{array}{c} \diagdown \\ \diagup \end{array} \begin{array}{c} OH \\ C_6H_5 \end{array}$ , m.p. 107°. The latter, an analogue of triphenylcarbinol (p. 528), is obtained from fluorenone by the action of phenyl magnesium bromide, or by the oxidation of 9-phenylfluorene with chromic acid. It gives highly coloured double salts, and a highly coloured perchlorate. It condenses with aniline hydrochloride to *p*-amino-diphenyl-fluorene, or *p*-amino-diphenyl-diphenylene-methane,  $(C_6H_5)_2C(C_6H_5)C_6H_4NH_2$ , m.p. 179°, and with phenol and sulphuric acid to give *p*-hydroxy-diphenyl-fluorene, m.p. 191° (*Ullmann*, *Ber.* 37, 73). By the action of phosphorus pentachloride, acetyl chloride, or gaseous hydrogen chloride, it gives 9-phenyl-9-chlorofluorene,  $(C_6H_5)_2CClC_6H_5$ , m.p. 79°, which, like triphenyl-chloromethane, is characterised by the mobility of its chlorine atom. When heated with copper powder in benzene solution it gives diphenyl-bifluorene, diphenylene-diphenylene,  $(C_6H_5)_2(C_6H_4)_2C \cdot C(C_6H_5)_2(C_6H_5)_2$ , m.p. 254°, which is analogous in structure to hexaphenylethane, but is considerably more stable. It forms colourless crystals, which in the cold give a colourless solution, but on warming, the solution becomes dark-brown owing to partial decomposition into two mols. of phenyl-fluorenyl, diphenylene-phenylmethyl,  $(C_6H_5)_2C(C_6H_5)$



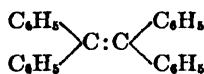
(Vol. IV). In the air it slowly passes into the peroxide, m.p.  $193^{\circ}$ , with absorption of oxygen. Even more stable is **dibiphenyl-bifluorene**, or **dibiphenylene-dibiphenylethane**,  $(C_6H_5)_2(C_6H_4 \cdot C_6H_4)_2C \cdot C(C_6H_4 \cdot C_6H_4)(C_6H_5)_2$ , m.p.  $176^{\circ}$ , obtained from 9-biphenyl-9-chlorofluorene,  $(C_6H_5)_2CClC_6H_4 \cdot C_6H_5$ , m.p.  $139^{\circ}$ . It undergoes slight dissociation in boiling anisole (Vol. IV), and is unaffected by oxygen in solution or in the solid state (*Schlenk*, Ann. 372, 21; *Ber.* 43, 1753). **9,9-Diphenylfluorene**,  $(C_6H_5)_2C(C_6H_5)_2$ , m.p.  $222^{\circ}$ , is obtained from diphenylmonobiphenyl-carbinol (*Ullmann*, *Ber.* 38, 4105).

**Diphenylmethyl-fluorene**, diphenylene-diphenylethane,  $(C_6H_5)_2CH \cdot CH(C_6H_5)_2$ , m.p.  $217^{\circ}$ , and **diphenylmethyle-fluorene**, diphenylene-diphenylethylene,  $(C_6H_5)_2C:C(C_6H_5)_2$ , m.p.  $229^{\circ}$  are obtained by decomposition of

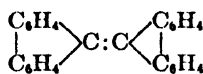
**diphenylene-diphenyl-succinic anhydride**,  $(C_6H_5)_2 \cdot C \cdot CO \begin{array}{c} \diagup \\ O \end{array} \begin{array}{c} \diagdown \\ C \cdot CO \end{array} (C_6H_5)_2$ , m.p.  $256^{\circ}$ , one of

the products of the action of cold conc. sulphuric acid on benzoic acid (p. 556). Diphenylene-diphenylethylene is also obtained by heating benzophenone chloride with fluorene. It forms colourless crystals, which dissolve to give a deep yellow solution. By careful oxidation of diphenylene-diphenylethylene with chromic acid, a pinacoline transformation takes place with the pinacone first formed, and **9,9-benzoyl-phenyl-fluorene**,  $(C_6H_5)_2C(C_6H_5)COC_6H_5$ , m.p.  $172^{\circ}$ , is obtained. This compound can also be obtained from potassium triphenylmethane or potassium 9-phenyl-fluorene by the action of benzoyl chloride, and is decomposed into 9-phenyl-fluorene and benzoic acid by alcoholic potash. When benzoyl-phenyl-fluorene is reduced with hydriodic acid and phosphorus an inverse pinacoline transformation occurs and ring extension, and 9,10-diphenylphenanthrene (p. 672) is formed (*Werner*, *Ber.* 37, 2887).

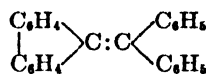
**Dibiphenylene-ethane**,  $(C_6H_5)_2CH \cdot CH(C_6H_5)_2$ , colourless needles, m.p.  $246^{\circ}$ , is obtained together with **dibiphenylene-ethylene**, or **bifluorene**,  $(C_6H_5)_2C:C(C_6H_5)_2$ , m.p.  $188^{\circ}$ , by heating fluorene with lead oxide. Bifluorene is also obtained by heating fluorene with bromine, chlorine, or sulphur, and by the action of methyl alcoholic potash on 9-bromofluorene (*Thiele*, Ann. 376, 271), and by the action of copper powder on fluorenone dichloride (*Ber.* 43, 1796) or bifluorenyl disulphide (*Bergmann*, Ann. 483, 79). It forms beautiful red needles, and gives a colourless addition product with bromine, which when heated with sodium in xylene re-forms the red hydrocarbon (*Grabe*, *Ber.* 25, 3146; Ann. 290, 238; 291, 1). In connection with the colour of highly condensed hydrocarbons, the following is of interest:



**Tetraphenylethylene**  
(p. 574); colourless



**Dibiphenylene-ethylene;**  
red needles



**Diphenylene-diphenyl-ethylene;** colourless;  
yellow in solution

*Cf.* also the yellow colour of acenaphthylene, and the red colour of diphenylfulvene.

**Fluorene-alcohol**, fluorenol,  $(C_6H_4)_2CHOH$ , m.p.  $158^{\circ}$ , is obtained by the action of sodium amalgam on the ketone, and from sodium diphenylene-glycollate on heating to  $120^{\circ}$ . It can also be obtained by the action of potassium ethylate and copper at  $200-240^{\circ}$  on 9-bromofluorene. **2-Hydroxyfluorene**, m.p.  $138^{\circ}$ , is formed from 2-bromofluorene in the same way (*Wiand*, Ann. 443, 132; 457, 249). **Retene**-, **chrysene**-, and **picene-fluorene-alcohol**, m.p.  $134^{\circ}$ ,  $167^{\circ}$  and  $230^{\circ}$  respectively, are obtained in the same way. **Fluorene-ether**,  $[(C_6H_4)_2CH]_2O$ , m.p.  $228^{\circ}$ , is obtained from 9-chlorofluorene and silver oxide (*Kliegl*, *Ber.* 43, 2490). **Ethyl-** and **benzyl-fluorenol**,  $(C_6H_4)_2C(OH)R$ , m.p.  $101^{\circ}$  and  $139^{\circ}$ , respectively, are obtained from fluorenone by the action of the corresponding alkyl magnesium halides (*Ullmann*, *Ber.* 38, 4105).

**Dibenzofulvene**, biphenylene-ethylene, 9-methylene-fluorene, m.p.  $53^{\circ}$ , is obtained by removal of water from 9-methyl-fluorenol, from (fluorenyl-9-methyl)-methane by distillation with calcium oxide, or from dibromo-biphenyl-ethylene and zinc. It is very unstable, and readily polymerises when exposed to light.

Remarkably enough, 2,7-dibromodibenzofulvene is more stable, and  $\omega$ -methyl-2,7-dibromodibenzofulvene can be kept indefinitely (*Sieglitz*, Ber. 55, 2032; *Wieland*, Ber. 55, 3313; *Ferrer*, An. soc. espan. fis. quim. 20, 459; C. 1923, III, 1161). The dibromide of dibenzofulvene gives dibiphenylene-butadiene, bi-dibenzofulvene, with dimethylaniline (*Wieland*, Ann. 443, 138).

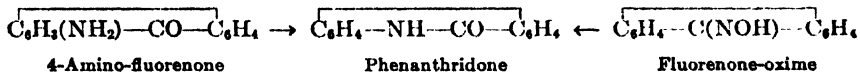
2-Acetyl-fluorene, m.p. 132°, is obtained by the action of acetyl chloride and aluminium chloride on fluorene at 0°; at 20–25° the product is 2,7-diacetyl-fluorene, m.p. 182–184°, crystallising in bright yellow needles, together with some 1,2-diacetyl-fluorene, m.p. 188°. If the reaction temperature is further increased, the only product is the 1,2-compound (*Dziewonski*, Bull. acad. polon. sci. lett. 1930, 529; Roc. Chem. 12, 167).

Fluorenone, diphenylene-ketone, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CO, m.p. 84°, b.p. 341°, is obtained from diphenic acid, isodiphenic acid, and *o*-diphenyl-carboxylic acid (pp. 505, 506) by heating with lime. It is also obtained by treating fluorene with sodium dichromate and glacial acetic acid, and by heating phenanthraquinone with soda-lime (*Anschütz*, Ann. 196, 45; *Graebe*, Ann. 279, 257; *Huntress*, Am. 53, 2720). It can also be obtained by boiling the diazonium compound of *o*-amino-benzophenone (p. 678) with water. Some of the substituted fluorenone are obtained by the same method (*Staedel*, Ber. 28, 111; *Ullmann*, Ber. 31, 1694). When oxidised with permanganate phthalic acid is formed, and *o*-phenyl-benzoic acid is produced when fluorenone is fused with alkali. Oxime, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C:NOH, m.p. 193°; phenylhydrazone, m.p. 151° (*Kirp*, Ber. 29, 230; *Goldschmidt*, Mo. 16, 807). Fluorenone dichloride, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CCl<sub>2</sub>, m.p. 99°, is obtained by the action of phosphorus pentachloride on fluorenone (*Schmidt*, Ber. 43, 1796).

3-Methyl-fluorenone, m.p. 68°, is obtained by the action of nitrous acid on *o*-aminophenyl-*p*-tolyl ketone. On reduction it gives 3-methyl-fluorene, m.p. 88° (*Sieglitz*, Ber. 54, 2070).

Fluorenone gives a loose addition product, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CO·NO<sub>2</sub>H, with concentrated nitric acid in the cold. This readily breaks down again into its components. With energetic nitration 2,7-dinitro- and 2,4,7-trinitro-fluorenone, m.p. 290° and 181°, are formed (*Schmidt*, Ber. 38, 3758; *Bell*, J. 1928, 1990). With fuming nitric acid and sulphuric acid, 2,3,6,7-tetranitro-fluorenone, m.p. 248°, is formed. 2,5-Dinitro-fluorenone, m.p. 241°, is formed by the oxidation of 2,5-dinitro-fluorene with chromic acid.

Hydroxy-fluorenone, 1-hydroxy-diphenylene ketone, C<sub>6</sub>H<sub>5</sub>(OH)·CO·C<sub>6</sub>H<sub>5</sub>, m.p. 115°, is obtained, together with xanthone, by boiling the diazonium compound of *o*-diamino-benzophenone with water (*Heyl*, Ber. 31, 3034), and from 1-amino-fluorenone, m.p. 110°, which is obtained by the action of potassium hypobromite on fluorenone-1-carboxylamide (*Goldschmidt*, Mo. 23, 886). 1-Hydroxy-fluorenone forms yellowish- or dark-red alkali salts, which have weak dyeing properties. It is converted into *o*-phenyl-salicylic acid, C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>3</sub>(OH)·COOH, by fusion with alkali (p. 504), and this substance condenses again to hydroxy-diphenylene-ketone when treated with concentrated sulphuric acid (*Staedel*, Ber. 28, 112). The isomeric 4-hydroxy-fluorenone, m.p. 249°, is obtained from 4-amino-fluorenone, m.p. 138°, which is itself obtained by the action of bromine and caustic potash on fluorenone-4-carboxylic amide. When 4-aminofluorenone is fused with alkali it is converted into phenanthridone. Phenanthridone is also formed by the Beckmann transformation from the oxime of fluorenone by heating with zinc chloride (*Kirp*, Ber. 29, 230):

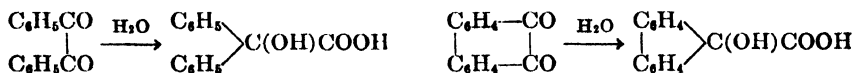


2-Amino-fluorenone, m.p. 163°, is obtained from 2-nitro-fluorenone, m.p. 222–223°, the oxidation product of 2-nitro-fluorene (p. 679), by reduction with ammonium sulphide. On diazotisation it gives 2-hydroxy-fluorenone, m.p. 210–211° (*Diels*, Ber. 34, 1764). 3-Hydroxy-fluorenone, m.p. 229° is obtained from 3-hydroxy-fluorenone-4-carboxylic acid (obtained synthetically) by splitting off carbon dioxide. 3-Amino-fluorenone, m.p. 158°, is obtained from 3-nitro-fluorenone, m.p. 232°. Diamino-fluorenone are obtained by reduction of the corresponding nitro-fluorenone. 2,3-Diamino-fluorenone, m.p. 185°, 2,5- and

**2,7-diamino-fluorenones**, m.p. 260–261°, and above 300°, respectively (*Courtot*, *Ann. chim.* [10], 14, 5; *Bardou*, *An. asoc. quim. Argentina* 19, 117). For **chloro- and bromo-fluorenones**, see *Courtot*, *Ann. chim.* [10], 14, 5; *Bull.* [4], 41, 58; *C.r.* 184, 1179.

**Carboxylic acids:** **9-(*ms*-)-Fluorene-carboxylic acid**, diphenylene-acetic acid,  $(C_6H_5)_2CHCOOH$ , m.p. 222–225°, is obtained by reducing diphenylene-glycolic acid with hydriodic acid and phosphorus, and by the action of benzene and aluminium chloride on ethyl trichloroacetate (*Delacre*, *Bull.* [3], 27, 875). It is also obtained by the action of benzene and aluminium chloride on benzoic acid, and from benzoyl chloride, benzene, and aluminium chloride by isomerisation (*Vorländer*, *Ber.* 44, 2466; 46, 1793). Solutions of its salts decompose giving fluorene, and, in the presence of air, fluorenone (*Wislicenus*, *Ber.* 46, 2770). Fluorene-9-carboxylic ester is a useful starting material for the preparation of 9-substituted fluorenes. It forms a compound with sodium, which readily reacts with alkyl halides, and by subsequent decarboxylation the 9-alkyl-fluorenes are obtained. **Fluorene-9-carboxylic ethyl ester**, m.p. 44–45°; **9-allyl-fluorene**, an oil, b.p. 175–176° (15 mm.); **9-benzyl-fluorene**, m.p. 134–135°, *etc.*, see *Wislicenus*, *Ber.* 46, 2772.

**9-(*ms*-)-Hydroxy-fluorene carboxylic acid**, diphenylene-glycolic acid,  $(C_6H_5)_2C(OH)COOH$ , m.p. 167°, is obtained by oxidising sodium diphenylene-acetate, or by boiling phenanthraquinone with caustic soda. It undergoes a similar transformation as the conversion of benzil into benzoic acid (p. 556), or of 1,2-naphthaquinones into hydroxy-indene carboxylic acids (p. 631)



The acid is oxidised by chromic acid to fluorenone. Analogous acids are obtained from retene- and chrysene-quinones (p. 694), and other substituted phenanthraquinones (*Schmidt*, *Ber.* 38, 3737). *ms*-Hydroxyfluorene carboxylic acid condenses with phenols and phenolic ethers in the presence of stannic chloride in just the same way as benzoic acid (p. 556), giving substituted **fluorene-phenyl carboxylic acids** (*Bistrzycki*, *Ber.* 43, 2496). It forms **fluorenechlorocarboxylic acid chloride**, m.p. 112°, with phosphorus pentachloride, which, on treatment with zinc filings in ether solution gives **diphenylene-ketene**,  $(C_6H_5)_2C:CO$ , in golden yellow spangles, m.p. 90° (*Staudinger*, *Ber.* 39, 3062).

**Fluorene-2-carboxylic acid**, m.p. 260° (decomp.), is obtained by the action of sodium amalgam and ethyl chlorocarbonate on 2-bromofluorene (*Loevenich*, *J. pr.* (2), 127, 248). **Fluorene-3-carboxylic acid**, m.p. 283–286°, is obtained by oxidation of 3-methyl-fluorene (*Sieglitz*, *Ber.* 54, 2070).

**Fluorene-oxalic acid**,  $(C_6H_5)_2CH \cdot COCOOH + H_2O$ , m.p. 150–151°, breaks down on heating into carbon monoxide, carbon dioxide, and fluorene. Its ester, which is obtained from fluorene, ethyl oxalate, and sodium (p. 678), gives with sodium alcoholates and methyl iodide or ethyl iodide, **methyl- and ethyl-fluorene oxalic ester**; by hydrolysis of the latter **9-methyl-fluorene**,  $(C_6H_5)_2CHCH_3$ , m.p. 46–47°, and **9-ethyl-fluorene**,  $(C_6H_5)_2CHC_2H_5$ , m.p. 108°, b.p. 166° (13 mm.), are obtained (*Wislicenus*, *Ber.* 35, 759). The preparation of 9-alkyl-fluorenes from fluorene-oxalic ester is not very satisfactory, as part of the initial substance is always converted into fluorene. Fluorene-oxalic ester gives **fluorene-hydroxyacetic acid** when reduced by Clemmensen's method, and with sodium amalgam it gives **fluorene-hydroxyacetic ester**, m.p. 81–82°, from which, by hydrolysis and dehydration, **dibenzofulvene-carboxylic acid**,  $(C_6H_5)_2C=CH-COOH$ , m.p. 227–228°, is produced (*Sieglitz*, *Ber.* 54, 2133).

**Fluorenone-carboxylic acids:** 1- or  $\alpha$ -acid,  $\begin{array}{c} \text{CO} \\ | \\ \text{---} \end{array} \begin{array}{c} \text{COOH} \\ | \\ \text{---} \end{array}$ , m.p. 192–193°, is obtained by oxidation of fluoranthene (p. 689) with chromic acid (*Goldschmidt*, *Mo.* 23, 886), by heating isodiphenic acid with concentrated sulphuric acid, or from 2'-aminobenzophenone-2-carboxylic acid by the action of nitrous acid (*Meyer*, *Ber.* 54, 347; *Sieglitz*, *Ber.* 57, 316). When reduced with sodium

amalgam it gives 1-fluorene-carboxylic acid,  $\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{COOH}$ , m.p.  $245^\circ$ , which gives fluorene when distilled with lime. The keto-acid gives isodiphenic acid when fused with alkali, and fluorenone when heated with lime. 4-,  $\gamma$ -, or

*o*-acid  $\begin{array}{c} \text{---CO---} \\ | \quad | \\ \text{---} \end{array}$ , m.p.  $227^\circ$ , is obtained by heating diphenic acid, and it is

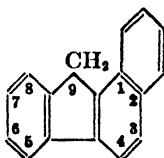
reconverted into the latter by fusion with alkali (*Graebe*, Ber. 20, 846; Ann. 247, 261). It can also be obtained together with *o*-benzoyl-fluorenone, m.p.  $95^\circ$ , by treating diphenic anhydride with aluminium chloride and benzene (*Gölz*, Mo. 23, 27).

Fluorenone-1,7-dicarboxylic acid,  $\begin{array}{c} \text{HOCO} \quad \text{CO} \\ | \quad | \\ \text{---} \end{array}$ , is obtained by the action of permanganate on retene-quinone. It is a yellow powder which decomposes at  $270^\circ$  into carbon dioxide and fluorenone-2-carboxylic acid, m.p.  $275^\circ$ . On distillation with lime it gives diphenyl, and when its silver salt is heated it gives fluorenone. Further oxidation with permanganate gives a mixture of 1,2,3- and 1,2,4-benzene-tricarboxylic acids (*Bamberger*, Ann. 229, 158; *Fortner*, Mo. 25, 443; *Bucher*, Am. 32, 374).

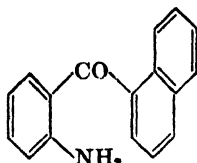
3-Hydroxyfluorenone-2-carboxylic acid,  $\begin{array}{c} \text{CO} \\ | \\ \text{---} \end{array}$ , m.p.  $278^\circ$ , is obtained synthetically by the action of caustic potash on indandione-methylenecacetoacetic ester (p. 599) (*Errera*, Gazz. 35, II, 539).

Because of their close relationship to fluorene, **chrysofluorene** and **picene-fluorene** will now be considered. They are related to chrysene (p. 692) and picene (p. 702) in the same way as fluorene is to phenanthrene. They are to be regarded as *o,o'*-methylene derivatives of 2-phenyl-naphthyl and 2,2'-dinaphthyl, respectively. They can also be called phenylene-naphthylene-methane and dinaphthylene-methane, respectively. They are formed by methods which correspond to those for fluorene.

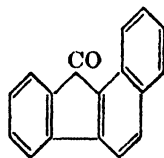
1,2-Benzofluorene, chrysofluorene, (I), m.p.  $188^\circ$ , is obtained by reduction of 1,2-benzofluorenone (*Graebe*, Ann. 335, 134) or by passing the vapour of benzyl-naphthalene through a red-hot tube (*Graebe*, Ber. 27, 953). An obvious synthesis starts with 3- $\beta$ -phenylethylindene, which gives tetrahydrochrysofluorene with aluminium chloride, and gives chrysofluorene on dehydrogenation with selenium.



(I)



(II)

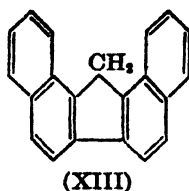


(III)

1,2-Benzofluorenone, chrysoketone, (III), m.p.  $132.5^\circ$ , is obtained by distillation of chrysoquinone with litharge (*Bamberger*, Ber. 23, 2439), and synthetically from *o*-1-naphthoyl-aniline (II) by boiling the diazo-compound (Ber. 29, 826).

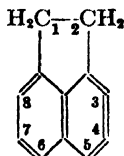
2,3-Benzofluorene (VI), m.p.  $208^\circ$ , is obtained by reducing 1,2-benzofluorenone (V) (*Thiele*, Ann. 376, 276). This ketone, m.p.  $152^\circ$ , is obtained by condensation of  $\alpha$ -hydrindone (IV) with phthalaldehyde (*Thiele*, Ann. 369, 287). 2,3-Benzofluorene can also be obtained by the action of aluminium chloride on  $\gamma$ -fluoroyl-2-butyric acid, with subsequent reduction and dehydrogenation (*Koelsch*, Am. 55, 3885).





## 6. ACENAPHTHENE GROUP

**Acenaphthene**, or *peri*-ethylene-naphthalene, is a condensed system in which a naphthalene nucleus is fused with a hydrogenated five-membered ring in the *peri*-position. It melts at 95°, and boils at 277°, and is found in coal-tar. It is produced by pyrogenic con-



densation of 1-ethylnaphthalene, or a mixture of naphthalene and ethylene, or by the action of alcoholic alkali on 1-bromoethylnaphthalene,  $C_{10}H_7 \cdot CH_2 \cdot CH_2Br$ . Another synthesis starts with naphthalene which is condensed with oxalyl chloride by Friedel-Crafts method, to acenaphthaquinone-1,2. Acenaphthane is obtained from this by reduction of the semicarbazone (*Schönberg*, Ber. **54**, 2838). The position of the ethylene group in the 1,8-position is proved by the oxidation of the compound to naphthalic acid (p. 637).

Substitution takes place in the acenaphthene molecule most readily in the 5- and 6-positions. In unsubstituted acenaphthene these positions are equivalent. The constitution of acenaphthene derivatives is obtained by converting them into the corresponding substitution products of naphthalic acid. By the action of chlorine or bromine on acenaphthene, 5-chloroacenaphthene, m.p. 70°, and 5-bromoacenaphthene, m.p. 52° are obtained, together with tetrabromoacenaphthene, m.p. 169–170° (*Crompton*, J. **101**, 958; *de Fazi*, Atti. r. accad. Lincei [5], **32**, 1, 343). 3-Chloroacenaphthene, m.p. 76–77°, 3-bromoacenaphthene, m.p. 78°, 3-iodoacenaphthene, m.p. 87°, are obtained from 3-aminoacenaphthene (see below) (*Morgan*, J. Soc. Chem. Ind. London **49**, Trans. 413).

Nitration leads to 5-nitroacenaphthene, m.p. 104°, and in the absence of water to 3-nitroacenaphthene, m.p. 151°. On reduction these pass into 5-aminoacenaphthene, m.p. 108°, and 3-aminoacenaphthene, m.p. 81° (*Morgan*, J. Soc. Chem. Ind. London, **47**, 16). 1-Aminoacenaphthene, m.p. 135°, has been obtained by reduction of 1-acenaphthenone-oxime. 4-Aminoacenaphthene, m.p. 89°, see *Morgan*, J. Soc. Chem. Ind. London **44**, 493. On energetic nitration of acenaphthene, 5,6-dinitroacenaphthene, m.p. 220–224°, is obtained. When reduced it gives 5,6-diaminoacenaphthene, m.p. 160°. 4,5-Diaminoacenaphthene, see *Meyer*, Ber. **44**, 2858.

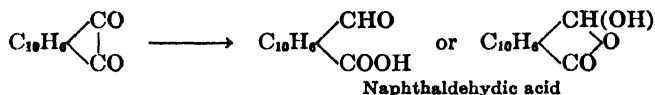
Sulphonation of acenaphthene at low temperatures leads to acenaphthene-5-sulphonic acid, and at higher temperatures the 3-sulphonic acid is obtained (*Dziewonski*, Bull. acad. polon. sci. lettres **1926**, 209). Acenaphthene-4-sulphonic acid is also known (*Dziewonski*, Bull. acad. polon. sci. lettres **1926**, 347).

**Acenaphthenol-1**, m.p. 148°, is obtained by oxidation of acenaphthene with lead dioxide, or by reduction of acenaphthenone-1 (*q.v.*) (*Tambor*, Helv. **9**, 463).

It readily splits off water and passes into acenaphthylene (*q.v.*). **Acenaphthenol-3**, m.p. 151°, see *Morgan*, J. Soc. Chem. Ind. London 49, 413.

Hydrogenation of acenaphthene with nickel and hydrogen leads to a mixture of **tetrahydroacenaphthene**, or tetraphthene, b.p. 240°, and **decahydroacenaphthene**, b.p. 235° (*Goswami*, C.r. 179, 1269).

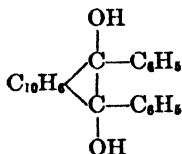
Oxidation of acenaphthene gives small quantities of **acenaphthene-quinone-1,2**, m.p. 281°, which is readily obtained by condensation of oxalyl chloride and naphthalene with aluminium chloride (*Schönberg*, Ber. 54, 2838). For homologous acenaphthene-quinones, see *Lesser*, Ber. 60, 242. The 1,2-quinone is reduced by zinc dust in glacial acetic acid to **acenaphthenone-1**, m.p. 121°, which can also be obtained from 1-naphthylacetyl chloride and aluminium chloride (Ger. Pat. 230,237). With alkali it passes into naphthaldehydic acid (*Graebe*, Ann. 276, 13; *Berend*, Ber. 32, 2103; Ger. Pat. 212,858):



The monoxime of acenaphthene-quinone,  $\text{C}_{12}\text{H}_6\text{O}(=\text{NOH})$ , m.p. 230°, gives naphthalimide on undergoing the Beckmann transformation (*Francesconi*, Gazz. 33, I, 36).

Acenaphthene-quinone readily combines with aromatic hydrocarbons, amines, and phenols in the presence of condensing agents such as aluminium chloride or zinc chloride, to give **diaryl-acenaphthenones** of the formula,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{C(R)}_2 \end{array}$

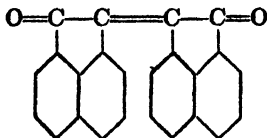
(*Zsuffa*, Ber. 43, 2915). **1,1-Diphenyl-acenaphthenone**,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{C(C}_6\text{H}_5)_2 \end{array}$ , m.p. 174°, is obtained from **1,2-diphenyl-acenaphthene-glycol**:



m.p. 156°, the reaction product of phenyl magnesium bromide and acenaphthene-quinone, after undergoing the pinacoline transformation in the presence of concentrated hydrochloric acid. Acenaphthene-quinone condenses with indoxyl and thio-indoxyl to give a violet and red vat dye ("Ciba scarlet"), respectively (*Grob*, Ber. 41, 3331; Ger. Pat. 212,870):



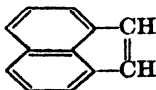
When reduced with hydriodic acid and phosphorus, acenaphthene-quinone-1,2 gives **biacenaphthylidene-dione**, **biacendione**,  $(\text{C}_{12}\text{H}_8\text{O})_2$ :



m.p. 293°, orange-red needles (*Graebe*, Ann. 276, 17). It is also obtained by removing hydrobromic acid from bromoacenaphthenone, or by condensation of acenaphthenone with acenaphthene-quinone in the presence of alkalis (*Graebe*, Ann. 290, 201; Ger. Pat. 212,870). **Biacenone**, m.p. 258°, golden-yellow needles, the ketone of the parent hydrocarbon, **biacene**, is obtained by boiling acenaphthylene

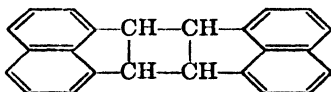
bromide with hydrochloric acid (*Dziewonski*, Ber. 58, 2542). With zinc dust and acetic anhydride, both ketones give the hydrocarbon **biacene**, which crystallises in golden-yellow tablets, melting at 271–273°.

If acenaphthene vapour is passed over red-hot lead oxide, or finely divided nickel, it is dehydrogenated, and **acenaphthylene** is formed:

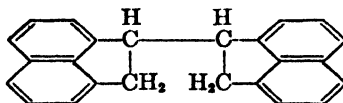


It forms yellow tablets, m.p. 92°, b.p. 270° (decomp.). When oxidised with chromic acid it breaks down to naphthalic acid (*Graebe*, Ber. 26, 2354). The most convenient method of preparing acenaphthylene is by passing acenaphthene vapour through a red-hot quartz tube (*Dziewonski*, Ber. 45, 2493). For a synthesis of substituted acenaphthylenes see *Thiele*, Ann. 369, 157.

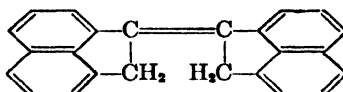
**Acenaphthylene**, like indene, shows a tendency towards polymerisation. When placed in sunlight it passes, in the course of a few days, into two colourless dimers, which are apparently *cis-trans* isomeric dinaphthylene-cyclobutanes,



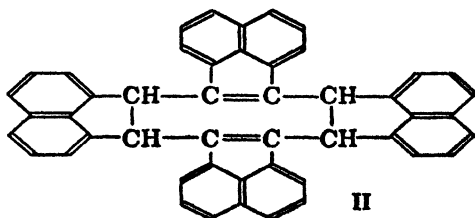
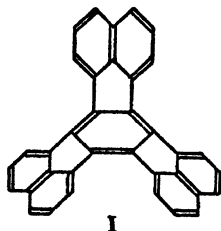
They are called  $\alpha$ -heptacycene and  $\beta$ -heptacycene, m.p. 307°, and 232–234°, respectively (*Dziewonski*, Ber. 45, 2491; 46, 1986). When reduced with hydriodic acid and phosphorus with heptacyclenes give 1,1'-**biacenaphthyl**, or *n*-dinaphthylene-butane:



m.p. 120° (*Dziewonski*, Ber. 47, 2685). A different type of polymerisation is shown by acenaphthylene with hydrochloric acid in glacial acetic acid. It forms **diacenaphthylidene**:

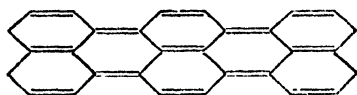


in golden-yellow leaflets, m.p. 277°, and higher polymers. On reduction it passes into dinaphthylene-butane (*Dolidski*, Ber. 48, 1917). On heating acenaphthylene to 100°, a mixture of highly polymerised hydrocarbons is formed. If heated to 280–290°, two crystalline substances can be isolated from the reaction mixture, one being **decacycene**, or trinaphthylene-benzene (I), m.p. 387°, and the other **fluorocyclene**, m.p. 395–396° (II) (*Dziewonski*, Ber. 36, 962; 47, 1679), which can also be obtained by the oxidation of acenaphthene with lead dioxide (Ber. 58, 729). For hydro-, hydroxy- and sulphonic derivatives of decacycene, see *Dziewonski*, Bull. acad. polon. sci. lettres 1923, 17, 165; *von Braun*, Ber. 67, 214.

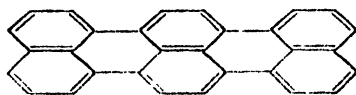




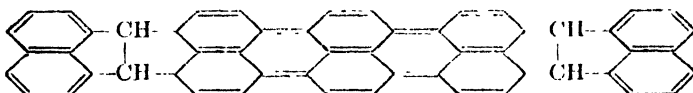
Other multinuclear systems are formed as by-products in the pyrogenic conversion of acenaphthene into acenaphthylene. **Rhodacene**,  $C_{30}H_{16}$  (possibly Ia), m.p. 338–340°; **leucacene**,  $C_{34}H_{22}$ , m.p. 250° (formula IIIa?), and **chalkacene**,  $C_{30}H_{16}$ , m.p. 358–360° (formula IIIa?) have been isolated. Leucacene and rhodacene are partially converted into chalkacene on heating. At the same time, other polyacenaphthylenes, such as **chromacene** are formed. These hydrocarbons are generally highly coloured.



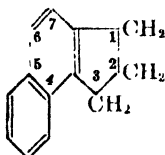
(Ia)



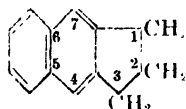
(IIIa)



If a five-membered ring is attached to the naphthalene nucleus in the 1,2- or 2,3-position, 4,5- or 5,6-**benzohydrindene** (I, II, below) is formed. 4,5-Benzohydrindene,  $C_{13}H_{12}$  (I), b.p. 146° (6 mm.) is obtained by the reduction of 4,5-benzohydrindone-3, m.p. 103°, which can be prepared from  $\beta$ -2-naphthylpropionic acid and stannic



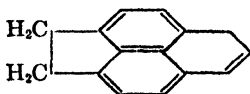
(I)



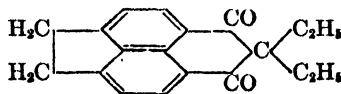
(II)

chloride (Mayer, Ber. 55, 1855; Kon, J. 1933, 1081; Cook, J. 1933, 1098). Derivatives of 5,6- and 4,5-benzindandione-1,3 have also been obtained by the condensation of naphthalene with dimethyl- and diethyl-malonyl chloride and aluminium chloride (Freund, Ann. 373, 299; 399, 190; 402, 54). If tetraline is used in place of naphthalene, the corresponding tetrahydro-derivatives are obtained (Fleischer, Ber. 53, 931).

By attaching the five-membered ring in the *peri*-position of *peri*-benzonaphthalene, *peri*-benzoacenaphthene (III) is formed.



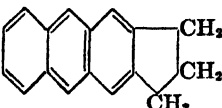
(III)



(IV)

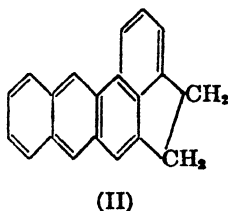
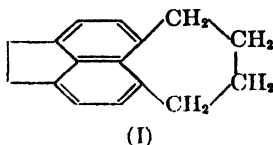
It was formerly known as *peri*-acenaphthindane. Derivatives of this hydrocarbon are known, and have been obtained by condensation of dimethyl- and diethyl-

malonyl chloride with acenaphthene. 2,2'-Diethyl-dihydro-*peri*-benzoacenaphthene-dione-1',3' (IV) has been obtained in this way. When treated with hydriodic acid and phosphorus, 2,2'-diethyl-dihydro-*peri*-benzoacenaphthene, m.p. 93-95°, is obtained (*Freund*, Ann. 373, 323; 399, 191; 402, 70; *Fleischer*, Ber. 53, 931).

*lin*-Hydrindanthracene, , m.p. 242-243°, is obtained by

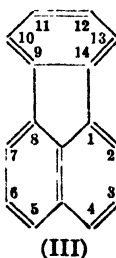
reducing hydrindanthraquinone, m.p. 180-181°, with zinc and ammonia. The latter is obtained from hydrindoyl-benzoic acid, together with an isomeric hydrindanthraquinone, by the action of concentrated sulphuric acid. Hydrindoyl-benzoic acid has been obtained from hydrindene and phthalic anhydride (*von Braun*, Ber. 53, 1165).

An acenaphthene with an attached seven-membered ring has been obtained from  $\beta$ -(5-acenaphthoyl)-propionic acid by heating with aluminium chloride and sodium chloride, and subsequent reduction by Clemmensen's method of the diketone produced intermediately (*Fieser*, Am. 54, 4347).



**Acenaphthanthracene** (II), m.p. 192°, yellow tablets, has been obtained from 4-acenaphthyl-phenylmethane-2'-carboxylic acid by condensation with zinc chloride and reduction of the anthrone produced (*Cook*, J. 1930, 1087).

A tetracyclic compound composed of three benzene rings and a five-membered ring is **fluoranthene** or **idryl** (III), which is found in the highest boiling fraction of coal-tar.



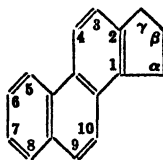
**Fluoranthene**,  $C_{16}H_{10}$ , m.p. 110°, b.p. 250° (60 mm.), picrate, m.p. 185°, has been obtained synthetically from  $\beta$ -9-fluorenyl-propionyl chloride. This compound is converted into 4-keto-1,2,3,4-tetrahydrofluoranthene, m.p. 98°, by aluminium chloride, and this gives 1,2,3,4-tetrahydrofluoranthene after Clemmensen reduction. On dehydrogenation this gives fluoranthene. This synthesis confirms the constitution of fluoranthene (*von Braun*, Ber. 62, 145). For the spectrochemistry of fluoranthene, see *Auwers*, Ann. 443, 187.

Fluoranthene is oxidised by chromic acid to 3,4-fluoranthene-quinone,  $C_{16}H_8O_2$ , m.p. 188°, which on further oxidation is converted into fluorenone-1-carboxylic acid (*Fittig*, Ann. 200, 1; *Mayer*, Ber. 46, 2579). By reduction of fluoranthene with sodium amalgam, or synthetically 1,2,3,4-tetrahydrofluoranthene,  $C_{16}H_{14}$ ,

m.p.  $74^{\circ}$ , is formed. With sodium in amyl alcohol, fluoranthene gives 1,2,3,4,9,10,11,12,13,14-decahydrofluoranthene,  $C_{18}H_{20}$ , b.p.  $181-183^{\circ}$  (12 mm.), and with hydrogen and nickel under pressure, perhydrofluoranthene,  $C_{18}H_{22}$ , b.p.  $168-170^{\circ}$  (12 mm.) (von Braun, Ber. 63, 2610).

Monosubstitution takes place in fluoranthene at positions 4 and 12. 4-Bromofluoranthene, m.p.  $103^{\circ}$ ; 4-aminofluoranthene, m.p.  $111-112^{\circ}$ ; 12-aminofluoranthene, m.p.  $168-169^{\circ}$ ; 4-hydroxyfluoranthene, m.p.  $186-187^{\circ}$ ; fluoranthene-12-carboxylic acid, m.p.  $183-185^{\circ}$ . For other derivatives, see von Braun, Ann. 488, 111; 496, 170.

1,2-Cyclopentenophenanthrene,  $C_{17}H_{14}$ , m.p.  $135^{\circ}$ , picrate, m.p.  $136^{\circ}$ , is important because of the existence of a similar skeleton in the sterols.



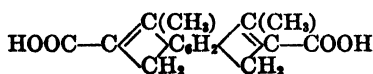
The synthesis starts from naphthyl-ethyl magnesium chloride, which reacts with cyclopentanone. Ring closure is effected with sulphuric acid, which also brings about simultaneous dehydrogenation to 1,2-cyclopentenophenanthrene (Ruzicka, Helv. 16, 833; Kon, J. 1933, 1081; Cook, J. 1933, 1098). 7-Methoxycyclopentenophenanthrene, m.p.  $136-137^{\circ}$ , picrate, m.p.  $137^{\circ}$ , has been obtained by dehydrogenation of derivatives of the follicular hormone, and also synthetically (Cohen, J. 1934, 653). The three methyl derivatives with the  $CH_3$  group in the five-membered ring have also been synthesised. They are  $\alpha$ -methyl- and  $\beta$ -methyl-cyclopentenophenanthrene, m.p.  $76-77^{\circ}$ , and  $107^{\circ}$ , respectively (Kon, J. 1933, 1081; Cook, J. 1933, 1098) and  $\gamma$ -methyl-cyclopentenophenanthrene, m.p.  $124-125^{\circ}$ , picrate m.p.  $119-120^{\circ}$  (Ber. 66, 1302). The latter can also be obtained by dehydrogenation of sterols, bile acids, cardiac poisons, and the neutral sapogenins, by selenium.

Benzdiindene is the name given to the tri-cyclic combination of a benzene nucleus with two cyclopentene nuclei. The name indacene has also been proposed for this compound (III). Dimethyl-indacene-dicarboxylic acid (IV) is obtained from *m*-xylylene-diacetoacetic ester and 80 per cent sulphuric acid. Tetraketohydrindacene-dicarboxylic ester,  $ROOCH(CO)_2C_6H_2(CO)_2CH_2COOR$ , is obtained from ethyl pyromellitate, ethyl acetate and sodium (Ephraim, Ber. 34, 3779). Other derivatives of indacene have been obtained from hydrindene, diethyl-malonyl chloride, and aluminium chloride (Freund, Ann. 414, 20).

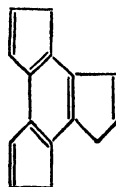
Derivatives of benztrihydrindene (V) are also known:



(III)



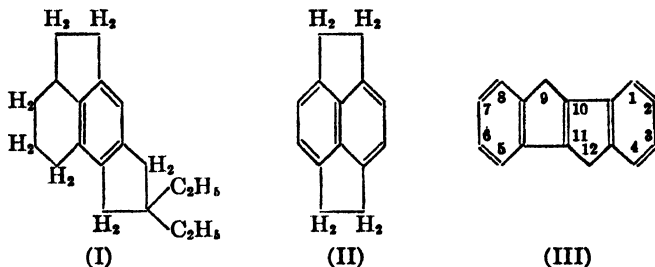
(IV)



(V)

(Freund, Ann. 414, 35).

Condensed systems with two six- and two five-membered rings can be obtained from tetraline, or better from tetrahydroacenaphthene and diethyl-malonyl chloride. The hydrocarbons are obtained from the ketones thus produced by Clemmensen reduction. 2,2-Diethyl-(tetrahydroacenaphth- $\alpha,\beta$ -hydrindene, b.p.  $190-195^{\circ}$  (16 mm.) (I):

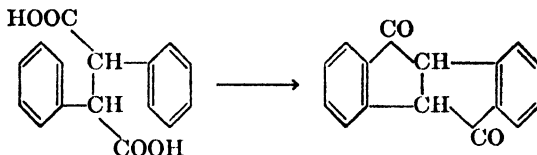


If the attachment of the second five-membered ring is in the *peri*-position, the ring system of **pyracene** (II) is produced.

**Pyracene-hemiquinone**, m.p. 226°, a derivative of this hydrocarbon, has been obtained from acenaphthene, oxalyl chloride and aluminium chloride (*Fleischer*, Ber. 53, 925).

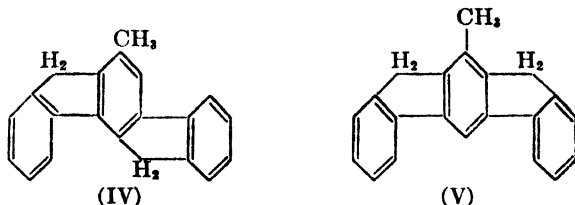
**Diphensuccindene** (III) is a condensed system of two indene molecules (*Brand*, Ber. 55, 601).

**Diphensuccindan**, m.p. 210°, is obtained from **diphensuccindandione-9,12** by replacing the oxygen with chlorine and reducing with zinc dust. **Diphensuccindandione-9,12** is obtained by condensation of diphenylsuccinic acid with concentrated sulphuric acid (*Reimer*, Ber. 14, 1806; *Roser*, Ann. 247, 153):

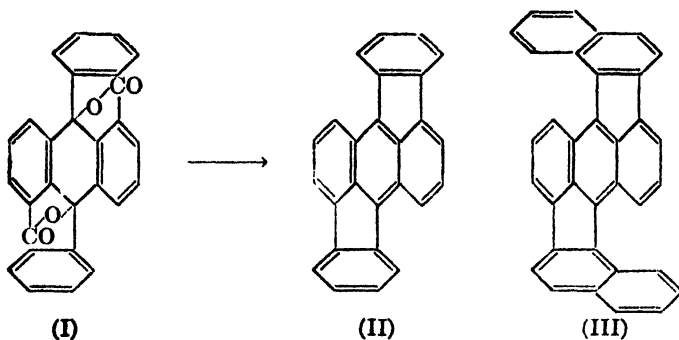


For further derivatives of diphensuccindene, see *Brand*, J. pr. 110, 1-26; Ber. 59, 1962.

**Phthalacene**,  $C_{21}H_{16}$ , m.p. 173° (IV) is formed by the reduction of phthalaconcarboxylic acid ester with hydriodic acid and phosphorus. The ester referred to is obtained by condensation of phthalic anhydride and acetoacetic ester (Ber. 17, 1389; *Errera*, Gazz. 37, II, 624; 38, II, 588). **Isophthalacene**,  $C_{21}H_{16}$  (V), yellow leaflets, m.p. 222°, and derivatives of phthalaconcarboxylic acid are dealt with in the same papers.

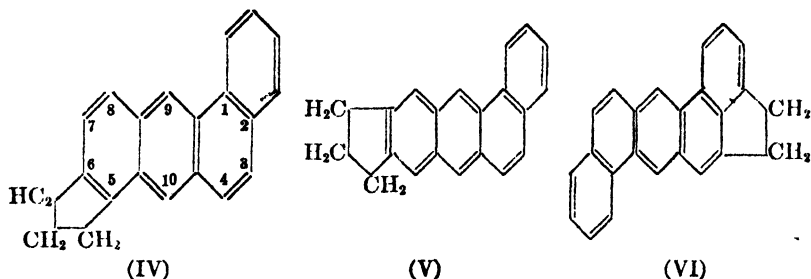


When fluorene is submitted to pyrogenic distillation through a quartz tube lined with copper or iron wire, biphenylene-phenanthrene (*q.v.*), **rubicene**, m.p. 306°, and **dihydrrubicene**, m.p. 296°, are formed (*Dziewonski*, C. 1923, I, 528; *Pummerer*, Ber. 45, 294; *Dziewonski*, Ber. 58, 2544; *Schlenk*, Ber. 61, 1675). Rubicene can also be obtained by heating fluorenone with calcium hydride. It forms fiery red needles, with an intense yellow fluorescence. The proof of the structure of rubicene (II) follows from its preparation from 9,10-diphenyl-9,10-dihydro-9,10-dihydroxy-anthracene-1,5-dicarboxylic lactone (I) by distillation with zinc dust in a current of carbon dioxide. Carbon dioxide is split off and disproportionation takes place (*Scholl*, Ber. 65, 926). For derivatives of rubicene, see *Dziewonski*, C. 1923, I, 528.



**Dioenzrubicene (III)**, dark-brown needles, is also known. It is obtained by a similar method to rubicene from the dilactone of 9,10-di- $\alpha$ -naphthyl-9,10-dihydroxy-9,10-dihydroanthracene-1,5-dicarboxylic acid (*Scholl, Ber.* 67, 1232).

**5,6-Cyclopenteno-1,2-benzanthracene (IV)**, m.p. 200°, picrate, m.p. 195°, is obtained by the condensation of hydrindene, 2-methyl-1-naphthoyl chloride and aluminium chloride. The ketone thus obtained is heated to 450°. An isomeric hydrocarbon, probably 6,7-cyclopenteno-1,2-benzanthracene (V) is formed at the same time.



It melts at 164–165°, picrate m.p. 180°. 5,6-Cyclopenteno-1,2-benzanthracene is carcinogenic and induces sexual characteristics in female rats from which the ovaries have been removed (*Cook, J.* 1931, 499, 2529; N. 21, 222; further condensed systems with the same action are also cited).

**Phenanthro-acenaphthene (VI)**, m.p. 231–232°, has been obtained from 5-(2-methyl-naphthoyl-1)-acenaphthene by heating to 430–450°. The derivative referred to is itself obtained from acenaphthene, 2-methyl-1-naphthoyl chloride and aluminium chloride (*Cook, J.* 1931, 499).

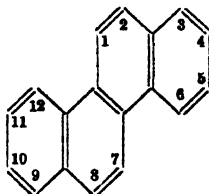
## 7. CONDENSED AROMATIC SYSTEMS WITH MORE THAN THREE SIX-MEMBERED RINGS

### (a) Systems with Four Rings

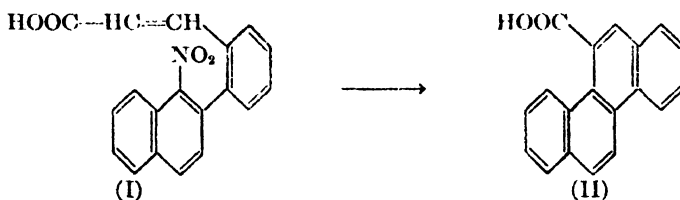
Aromatic ring systems with four condensed benzene nuclei, such as chrysene and pyrene, are found in the highest boiling fractions of coal-tar, but are largely made synthetically. The constitution of these substances is arrived at from their oxidation products, where the synthesis itself is not conclusive.

**Chrysene**, or 1,2-benzphenanthrene,  $C_{18}H_{12}$ , m.p. 251°, b.p. 448°, in the pure state forms silver-white leaflets with a violet fluorescence. In the impure state it is yellow in colour; hence the name

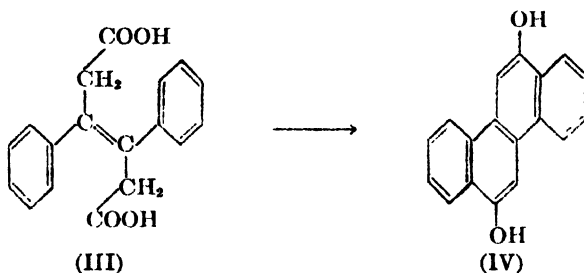
$\psi\rho\iota\sigma\epsilon\omicron\varsigma$  = golden yellow. The impurity which imparts this yellow colour to chrysene can easily be removed by treating the substance with maleic anhydride, with which chrysene itself does not combine (*Clar*, Ber. 65, 1411). Chrysene is found in the highest boiling fractions of coal-tar, and is also obtained by the dehydrogenation of sterols with palladium, carbon, selenium, or zinc dust (*Diels*, Ber. 60, 140; *Raudnitz*, Ber. 66, 879; *Diels*, Ann. 459, 1). The distribution of the double bonds in the molecule follows from the optical properties of the hydrocarbon, and from the fact the maleic anhydride will not combine with it:



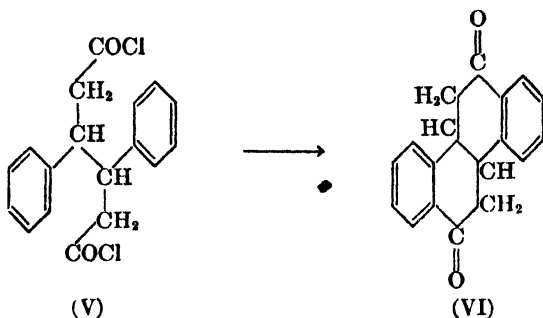
Chrysene has been obtained synthetically from phenyl-naphthyl-ethane,  $C_6H_5CH_2 \cdot CH_2C_{10}H_7$ , just as phenanthrene is obtained from dibenzyl (p. 668), and from coumarone and naphthalene. It is obtained in good yield by heating indene (p. 590) (*Spilker*, Ber. 26, 1544). A very interesting synthesis starts from 1-nitronaphthyl-2-*o*-cinnamic acid (I), which is converted into **chrysene-1-carboxylic acid** (II), m.p. 222–223°, through the amino-compound, diazotisation, and treatment of the diazo-compound with copper powder. Distillation of the acid (II) gives the hydrocarbon (*Weitzenböck*, Mo. 33, 549):



Another synthesis starts from  $\alpha, \alpha'$ -dihydro- $\beta, \beta'$ -diphenyl-muconic acid (III), m.p. 297°, which, on treatment with acetic anhydride and some sulphuric acid, gives the diacetyl derivative of **2,8-dihydroxychrysene** (IV), m.p. 246°. Chrysene is readily obtained from this compound with zinc dust.

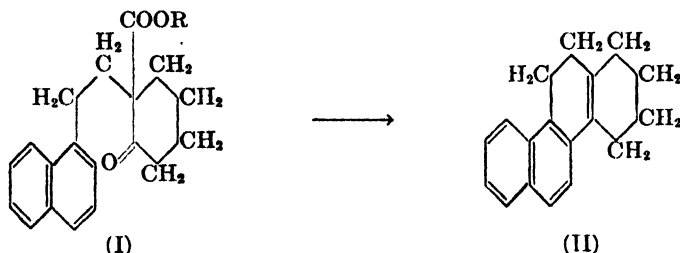


A diketone (VI), m.p. 295°, is obtained from diphenyl-adipyl chloride by intramolecular Friedel-Crafts synthesis:



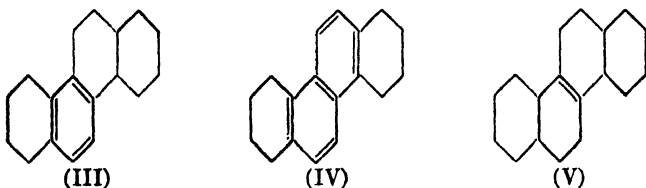
When this is reduced with hydriodic acid and phosphorus, a partly hydrogenated hydrocarbon is formed, which is converted into chrysene by passing over lead oxide (*von Braun*, Ber. 64, 2461).

Another synthesis of wide application depends on the condensation of  $\beta$ -(naphthyl-1-ethyl) bromide with cyclohexanone-*o*-carboxylic ester. The keto-ester (I) which is formed is cyclised by sulphuric acid (II), and the reaction product is dehydrogenated by selenium or palladinised-charcoal.



For substituted chrysenes, see *Abegg*, Ber. 24, 949.

When chrysene is catalytically hydrogenated with nickel and hydrogen under pressure, dodecahydrochrysene (III), m.p. 55–57°, b.p. 224–226°, is formed.

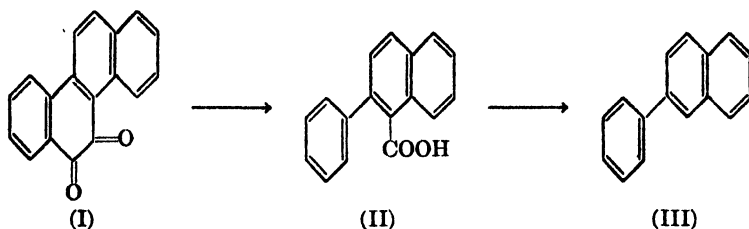


If the hydrogenation is carried out with selenium or sulphur, octahydrochrysene (IV), m.p. 138–140°, picrate m.p. 136–139° is formed, and by more energetic hydrogenation hexadecahydrochrysene (V), b.p. 168° (0.5 mm.), an oil, is formed.

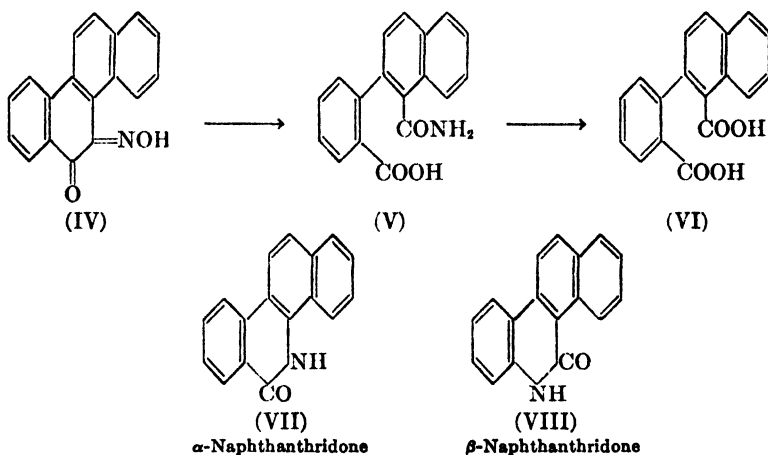
When chrysene is warmed with chromic acid in glacial acetic acid, chrysene-quinone,  $C_{18}H_{10}O_2$ , is formed in red needles, m.p. 235° (I). When this compound is distilled with lead oxide it is converted into chrysene-ketone,  $C_{17}H_{10}O$ , which can be reduced to chrysofluorene (*q.v.*).

When boiled with permanganate, both chrysene-quinone and chrysene-ketone give diphtallic acid,  $COOH \cdot C_6H_4 \cdot COCO \cdot C_6H_4 \cdot COOH$  (see p. 570). When heated with soda-lime or caustic potash and lead dioxide, chrysene-quinone gives chryseneic acid (II), or 2-phenyl-1-naphthoic acid (p. 635), which gives 2-phenyl-naphthalene by loss of carbon dioxide (III) (*Bamberger*, Ber. 26, 1745).

Chrysene-quinone oxime (IV), m.p. 161°, gives at 100°, two isomeric amides (V), m.p. 220° and 275°, respectively, which, on hydrolysis give chrysodiphenic acid (VI), m.p. 199°.

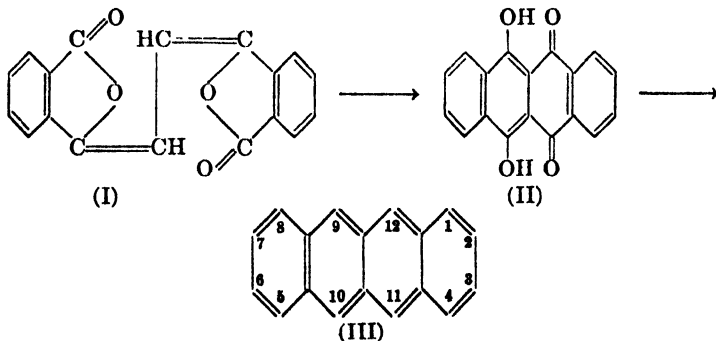


The diphenamine-acids (p. 506) are converted by sodium hypochlorite into  $\alpha$ - and  $\beta$ -naphthanthrindones (VII, VIII), m.p. 332° and 338° (*Graebe*, Ann. 311, 257; 335, 124; *Pschorr*, Ber. 35, 2744). Oxidation of 2,8-dihydroxychrysene gives *amphi-chrysene-quinone-2,8*, m.p. 288-290°. 8-Hydroxy-1,2-chrysene-quinone, see *Bischke*, Ann. 384, 174.



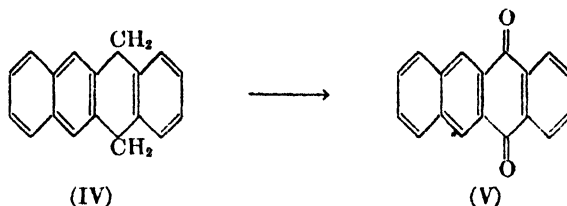
(*lin*-)2,3-Benzanthracene, or naphthacene (III), m.p. 335°, is orange in colour, and is obtained from its oxygen-containing derivatives, hydroxy- and dihydroxy-naphthacene-quinone by distillation with zinc dust. In comparison with anthracene it shows a greater tendency to pass into the stage of **dihydronaphthacene**.

**Dihydroxynaphthacene-quinone**, (II), m.p. 347°, forms red leaflets, and is obtained from "ethine-diphtalyl" (I) (pp. 587, 600) by treatment with sodium





methoxide, and by oxidation of diketohydrindene (p. 599) with potassium sulphate. When oxidised with nitric acid it forms **naphthacene-diquinone**, m.p.  $133^{\circ}$ , which very readily passes into dihydroxynaphthacene-quinone. When the latter is reduced with hydriodic acid and phosphorus, **dihydronaphthacene** (IV),  $C_{18}H_{14}$ , m.p.  $207^{\circ}$ , is formed, and this, when oxidised with chromic acid gives **naphthacene-quinone** (V), (2,3-benzanthraquinone) m.p.  $204^{\circ}$  (Gabriel, Ber. 31, 1272; 33, 446).



When phthalic anhydride is condensed with 1-naphthol and 1-hydroxy-naphthoyl-*o*-benzoic acid by means of boric acid and sulphuric acid, **10-hydroxynaphthacene-quinone**, m.p.  $303^{\circ}$ , is formed, which readily passes into the above-mentioned dihydroxynaphthacene-quinone on oxidation, and breaks down to naphthacene and dihydronaphthacene on reduction (Deichler, Ber. 36, 547, 710, 2326). When 2,3-naphthalene-dicarboxylic anhydride is condensed with benzene, 2-benzoyl-3-naphthoic acid is formed. This is converted into naphthacene-quinone when fused with a mixture of sodium chloride and aluminium chloride. Derivatives of this compound can also be obtained by this method (Waldmann, Ber. 64, 1713). Another method for the preparation of naphthacene-quinone is the dehydrogenation of 5,6,7,8,11,12-hexahydro-11,12-diketo-naphthacene ("tetral-2,3-anthraquinone") with bromine. This compound is easily obtained from *o*-(tetroyl-2-) benzoic acid (Schroeter, Ber. 54, 2242). When reduced with tin and glacial acetic acid, naphthacene-quinone gives the deep red hydroquinone, which slowly changes to 2,3-benzanthrone. The hydroquinone readily forms a peroxide with oxygen.

(ang-)1,2-Benzanthracene (VI),  $C_{18}H_{12}$ , m.p.  $158-159^{\circ}$ , picrate, m.p.  $141.5-142.5^{\circ}$ , is obtained from its quinone by warming with zinc dust and ammonia, and also from 1-benzyl-2-methyl-naphthalene by distillation with zinc dust, when some naphthacene is also formed (Dziewonski, Bull. acad. polon. sci. lettres 1927, 181). Another method of getting 1,2-benzanthracene starts from phenanthryl-butyric acid, which is converted by sulphuric acid into 1-keto-1,2,3,4-tetrahydro-5,6-benzanthracene, which gives 1,2-benzanthracene when reduced by Clemmensen's method, and dehydrogenated with selenium (Haworth, J. 1933, 1012). It forms an addition compound with maleic anhydride.

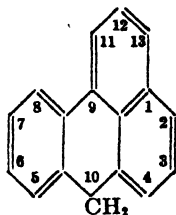


**1,2-Benzanthraquinone** (VII), Sirius yellow G,  $C_{18}H_8(CO)_2$ , m.p.  $169^{\circ}$ , is obtained from 1-naphthoyl-*o*-benzoic acid in the same way as anthraquinone is obtained from benzoyl-benzoic acid. 1,2-Benzanthraquinone is broken down into 2-naphthoic acid and benzoic acid on fusion with potash (Els, Ber. 19, 2209; Graebe, Ber. 29, 827; Gabriel, Ber. 33, 446). The reaction of naphthalene-1,2-dicarboxylic anhydride with benzene and aluminium chloride gives 1-benzoyl-2-naphthoic acid and 2-benzoyl-1-naphthoic acid, which both cyclise to the same 1,2-benzanthraquinone. The process can also be used with naphthalene, and then leads to derivatives of dibenzanthraquinone (pentacene) (Waldmann J. pr.

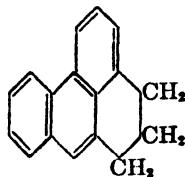
[2], 131, 71). 4-Bromo-1,2-benzanthraquinone, m.p. 231-232°. For further halogeno-1,2-benzanthraquinones, see *Johnson*, *Am.* 54, 3289.

Methyl-1,2-benzanthracenes are obtained from the corresponding substituted benzoyl chlorides, methyl-naphthalenes, and aluminium chloride in carbon disulphide at 0°, the ketones formed being converted into benzanthrane derivatives by heating to 420°. 6-Methyl-1,2-benzanthracene, m.p. 151°, is obtained from 1-*p*-toluyl-2-methylnaphthalene. 7-Methyl-1,2-benzanthracene, m.p. 182°, and others, see *Cook*, *J.* 1933, 1592; 1932, 456. Like the naphthanthracenes they are usually colourless. For methyl-1,2-benzanthraquinones, see *Scholl*, *Mo.* 32, 997; 41, 583. 1,2-Benz-3,4-anthraquinone is also known, m.p. 263°, red needles (*Fieser*, *Am.* 51, 3141).

A series of compounds of technical importance are derived from 1,9-benzanthracene, benzanthrene (I),  $C_{17}H_{12}$ , m.p. 84°, picrate m.p. 110-111°. It is obtained from benzanthrene (*q.v.*) or 1,10-trimethylene-9-hydroxyphenanthrene (see below) by reduction with zinc dust (*Bally*, *Ber.* 44, 1667). The arrangement of double bonds is



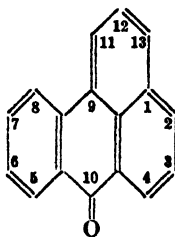
(I)



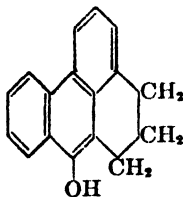
(II)

arrived at from the absorption spectrum of the compound, and its behaviour towards maleic anhydride (*Clar*, *Ber.* 65, 1425). Dihydro-benzanthracene, 1,10-trimethylene-phenanthrene, m.p. 81-83°, colourless needles (II), reacts, on the other hand, like a phenanthrene derivative, and does not react with maleic anhydride. It is obtained by the action of hydriodic acid and phosphorus on benzanthrene, and shows a violet-blue fluorescence.

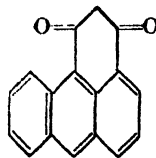
1,9-Benzanthrone (III), m.p. 75°, bright yellow needles, is formed by the action of glycerol and concentrated sulphuric acid at 100-110° on anthraquinone or, better, anthrone (*von Braun*, *Ber.* 38, 170).



(III)

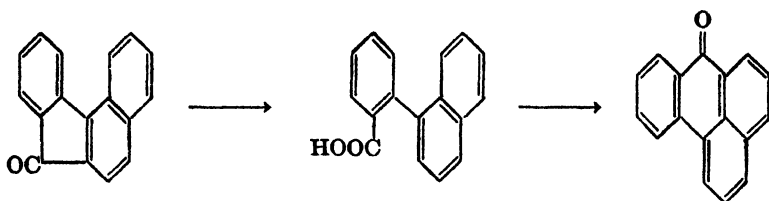


(IV)



(V)

Benzanthrene and substituted benzanthrenes can also be obtained by ring-closure of *o*-naphthyl-benzoic acids (obtained by fusion of 3,4-benzofluorenone with potash) (*Schaarschmidt*, *Ber.* 50, 294; 51, 1074):



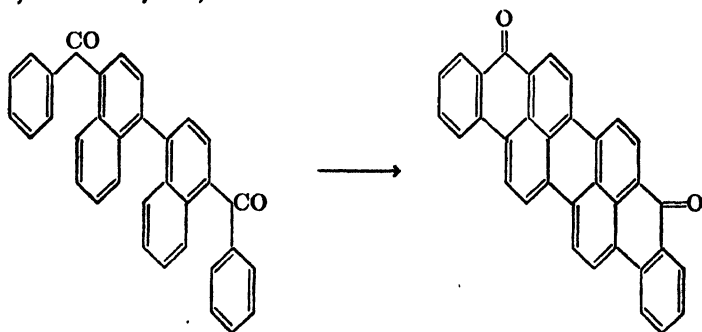
Another synthesis depends on the action of aluminium chloride on 1-naphthyl-phenyl ketone at  $140^{\circ}$  (*Scholl*, Ann. 394, 115). Alkylbenzanthrone are obtained by using alkylated naphthyl- or phenyl-nuclei. 2-5,6,7-Methyl-1,9-benzantrones, m.p.  $199^{\circ}$ ,  $167$ – $168^{\circ}$ ,  $169.5^{\circ}$  and  $155^{\circ}$  (see *Scholl*, Ann. 394, 145). 2,4-Dimethylbenzanthrone, m.p.  $165^{\circ}$ , 7-phenyl-benzanthrone, m.p.  $171^{\circ}$  yellowish-brown leaflets. For chlorobenzantrones, see *Scholl*, Ber. 55, 115. On nitration of benzanthrone, 12- and 13-nitrobenzantrones, m.p.  $298^{\circ}$  and  $244^{\circ}$ , respectively, are obtained, together with 6,13- and 8,13-dinitrobenzanthrone, m.p.  $268^{\circ}$  and  $236^{\circ}$ . 2-Aminobenzanthrone, m.p.  $223$ – $224^{\circ}$ , is obtained by the action of ammonia on 2-hydroxybenzanthrone (*q.v.*). For a synthesis of 6,13-diaminobenzanthrone, see U. S. Pat. 1,565,229.

2-Hydroxybenzanthrone, m.p.  $291^{\circ}$ , is obtained by heating benzanthrone with alkali and some potassium chlorate to  $230$ – $240^{\circ}$  (*Perkin*, J. 121, 474). Other hydroxybenzantrones have been obtained by the action of glycerol and sulphuric acid on the hydroxyanthraquinones (*Perkin*, J. 117, 696; 121, 474).

Reduction of benzanthrone with zinc dust and caustic soda gives rise to 1,10-trimethylene-9-hydroxyphenanthrene (IV), m.p.  $150$ – $151^{\circ}$  (*Clar*, Ber. 65, 1420). For products of catalytic hydrogenation, see *von Braun*, Ber. 58, 2673. A hydro-derivative (V) of benzanthrone is obtained by condensation of malonyl chloride with anthracene (*Kardos*, Ber. 46, 2090).

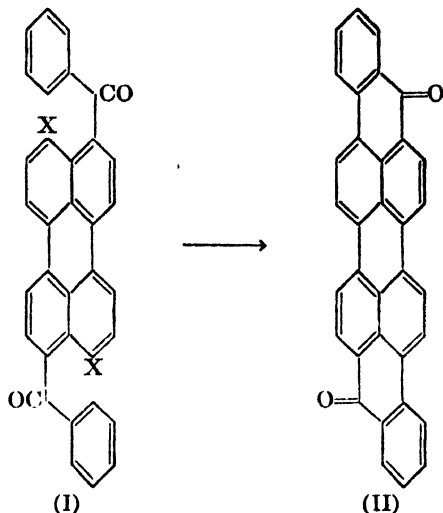
Benzanthrone-12-carboxylic acid,  $C_{17}H_{13}O_3$ , m.p.  $347^{\circ}$ , is obtained by ring closure of 1-phenylnaphthalene-2,3-dicarboxylic acid with phosphorus pentoxide (*Schaarschmidt*, Ber. 50, 294) or by the action of sulphuric acid on the anhydride of the acid at a higher temperature (*Schaarschmidt*, Ber. 51, 1074).

When the benzantrones (except hydroxy-, nitro-, and amino-benzantrones) are fused with potash, two molecules combine and give blue to violet vat dyes of the indanthrene group, which are very fast. These dyes include violanthrene and isoviolanthrene. The constitution of violanthrene is arrived at from its formation from 4,4'-dibenzoyl-1,1'-binaphthyl by heating with aluminium chloride (*Scholl*, Ann. 394, 129):



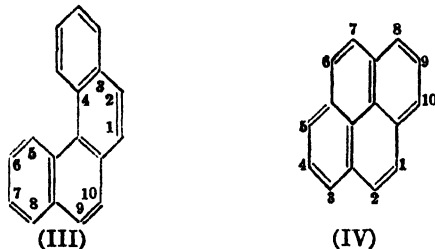
Isoviolanthrene, indanthrene violet R extra (II) is obtained from halogeno-benzantrones by fusion with potash (*Scholl*, Ann. 394, 129). Its constitution follows from its synthesis from 3,9-dibenzoyl-

perylene, which is converted into isoviolanthrone by treating its solution in concentrated sulphuric acid with mild oxidising agents (*Marschalk*, Bull. [4], 41, 706), or by heating it with aluminium chloride. It can also be obtained from 3,9-dibenzoyl-9,10-dihalogeno-perylene (I) by heating with alkali in boiling aniline or quinoline (*Zinke*, Ber. 58, 323, 799, 2222). These dyes can therefore be regarded as derivatives of perylene.



For the mechanism of their formation by fusion of benzanthrone with potash, which passes through the dibenzanthronyls, see *Lüttringhaus*, Ann. 473, 259; *Pongratz*, Mo. 62, 172.

3,4-Benzphenanthrene,  $C_{18}H_{12}$ , (III), m.p. 68°, picrate, m.p. 126–127°, is obtained by removing carbon dioxide from 3,4-benzphenanthrene-1-carboxylic acid, m.p. 240–241°, which is obtained from  $\alpha$ -(2-naphthyl)- $\beta$ -o-aminophenyl-acrylic acid by diazotisation and shaking with cuprous chloride (Ber. 51, 510). 1,2-Benzanthracene-4-carboxylic acid is obtained at the same time. It melts at 281–282°. 3,4-Benzphenanthraquinone forms ruby-red needles, m.p. 187–188° (*Cook*, J. 1931, 2524).

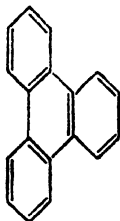


Pyrene (IV),  $C_{16}H_{10}$ , m.p. 150°, b.p. 260° (60 mm.), is found in coal-tar. It does not react with maleic anhydride and can thus be readily separated from the yellow impurities which frequently accompany it. For the spectrochemistry of pyrene, see *Auwers*, Ann. 443, 187; *Clar*, Ber. 65, 1425. It has been obtained synthetically by condensation of *peri*-benzonaphthalene (p. 640) with malonyl bromide, and subsequent distillation with zinc dust (*Fleischer*, Ber. 55, 3289), or from 1,4,5,8-naphthalene-tetracarboxylic acid by condensation of its anhydride

with diethyl malonate, followed by distillation with zinc dust (*Freund*, Ann. 402, 77). It can also be prepared by dehydrogenation of decahydropyrene with lead oxide. **Decahydropyrene** itself is obtained from hexahydrobenzo-naphthyl-propionic acid, ring closure with aluminium chloride, and Clemmensen reduction of the ketone (*von Braun*, Ber. 61, 962).

Pyrene is oxidised by chromic acid in glacial acetic acid to **pyrene-quinone**,  $C_{16}H_8O_2$ , which probably contains the  $O=$  groups in the 3,8 positions (*Scholl*, Ann. 394, 125). Further oxidation gives **pyrenic acid**,  $C_{16}H_8(CO)(COOH)_2$  (*Langstein*, Mo. 31, 861). This is a keto-dicarboxylic acid, and readily forms an anhydride and an imide (*Bamberger*, Ber. 19, 1997), and gives **pyrene-ketone**,  $C_{16}H_8(CO)$ , m.p.  $141^\circ$  on distillation. If pyrenic acid is oxidised with permanganate, 1,4,5,8-naphthalene-tetracarboxylic acid is formed, and if pyrene-ketone is subjected to the same treatment, naphthalic acid is obtained (p. 637). By acting on pyrenic acid with benzoyl chloride, **mono-**, **di-**, and **tri-benzoyl-pyrene**, 3,8-dibenzoyl-pyrene, m.p.  $158-160^\circ$ , and 3,5,8-tri-benzoyl-pyrene, m.p.  $239-240^\circ$ , are formed (*Scholl*, Ann. 394, 162).

9,10-Benzphenanthrene, or triphenylene,  $C_{18}H_{12}$ , forms white needles, m.p.  $198^\circ$ , obtained by passing benzene vapour through a red-hot tube. It does not react with maleic anhydride. It is oxidised by fuming nitric acid to mellitic acid (p. 397). A dodecahydrotriphenylene,  $C_{18}H_{24}$ ,

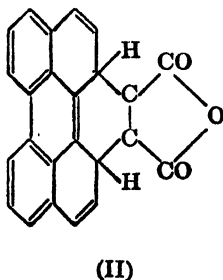
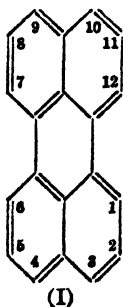


m.p.  $233^\circ$ , is formed by the condensation of cyclohexanone with methyl alcoholic sulphuric acid, in the same way as mesitylene is obtained from acetone (*Mannich*, Ber. 40, 153). For hexadeca- and perhydrotriphenylene, see *Schrauth*, Ber. 56, 2024.

### (b) Systems With Five Rings

**Perylene (I)**,  $C_{20}H_{12}$ , m.p.  $262-265^\circ$ , is a system with five condensed benzene rings. It forms leaflets with a bronze lustre, and is formed by the linking of two naphthalene nuclei in the *peri*-position on heating with aluminium chloride to  $140^\circ$ .

Its constitution follows from its formation from 1,8-diiodonaphthalene on heating with copper-bronze (*Scholl*, Ber. 43, 2202; *Weitzenböck*, Ber. 46, 1994). Another synthesis starts from the chlorophosphoric ester of 2,2'-dihydroxy-1,1'-



**dinaphthyl**, which on heating with condensing agents gives **1,12-dihydroxyperylene**. This can be reduced to perylene by means of zinc dust (*Hansging*, Mo. 40, 403; *Zincke*, Mo. 43, 125; *Marschalk*, Bull. [4], 43, 1388). Perylene can also be obtained by heating **2,2'-dihydroxy-1,1'-dinaphthyl** with metaphosphoric acid (*Uchida*, J. Soc. Chem. Ind. Japan 36, 222).

Perylene forms an addition product (II) with maleic anhydride. It crystallises in orange needles, decomposing at 265–270°. Only one molecule is taken up, and that is attached at the middle of the conjugated system. From this behaviour, the optical absorption, and the predominating formation of the 3,9-quinone on oxidation, the arrangement of double bonds in perylene shown above is confirmed (*Clar*, Ber. 65, 846).

Perylene dissolves in concentrated sulphuric acid with a deep green colour, which changes through bluish-green to blue, and then to reddish-violet. Sulphur dioxide is given off, and **perylene-3,10-quinone** and **perylene sulphonic acids** are formed (*Zincke*, Mo. 61, 1).

Substituents enter the perylene molecule chiefly in the 3,9-, 3,10-, or 3,4-positions. By the action of chlorine in the cold, only one chlorine atom substitutes hydrogen, and eight other chlorine atoms are added. In the hot, **hexachloro-perylene**, m.p. 356–357°, is formed (*Zincke*, Mo. 48, 746). **3,9-Dichloro-perylene**, m.p. 280–281°, is obtained from perylene and hydrogen chloride in glacial acetic acid. **3,4,9,10-Tetrachloro-perylene**, m.p. 350°, is obtained in the same way (*Zincke*, Ber. 58, 330). **3,9-Dichloro-perylene** is obtained by the action of aluminium chloride on perylene. No monochloro-perylene is known. For the corresponding **bromoperylene**s, see *Zincke*, Ber. 58, 323; 60, 579.

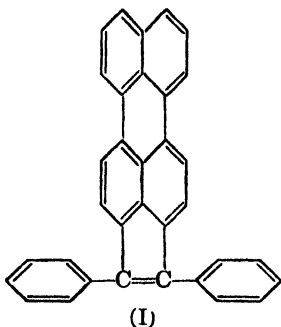
The nitration of perylene gives different products according to the conditions. **Mono-, di-, tri- and tetra-nitroperylene**s have been made (*Zincke*, Mo. 40, 406; Ber. 60, 580). The structure of di- and tetra-nitro-perylene is known. The former is the 3,10-compound, and the latter 3,4,9,10-**tetranitroperylene** (*Zincke*, Mo. 51, 205; *Funke*, Mo. 52, 3). Reduction of dinitro-perylene gives 3,10-**diamino-perylene**. Reduction of the tetra-nitro compound leads apparently to a quinone-like compound, **diamino-perylene-quinone-diimine**, and **tetra-amino-perylene** (*Zincke*, Mo. 51, 205; *Funke*, Mo. 52, 221). Reduction of 3,9-**dichloro-4,10-dinitroperylene** (obtained by nitration of 3,9-dichloro-perylene) gives 3,9-**dichloro-4,10-diamino-perylene**, which can be converted into 4,10-**diamino-perylene** by heating with aniline (*Funke*, Mo. 52, 1). Sulphonation of perylene gives rise to 3,9- and 3,10-**perylene disulphonic acids** (*Marschalk*, Bull. [4], 41, 74).

When perylene is treated with hydriodic acid at 250°, a **hexahydro-derivative**, m.p. 189°, is formed. Catalytic hydrogenation with palladium gives an **octahydro-perylene** (*Zincke*, Mo. 51, 280). Hydrogenation with sodium and amyl alcohol gives also an **octahydro-perylene**, m.p. 119–121°, together with  $\alpha$ - and  $\beta$ -**tetradecahydro-perylene**, m.p. 180–181.5° and 161–162°. These can also be obtained by more energetic catalytic hydrogenation (*Zincke*, Mo. 59, 241; *Uchida*, J. Soc. Chem. Ind. Japan 36, 222). For chlorohydroperylene, see *Zincke*, Mo. 48, 741.

Many **perylene-quinones** are known: **1,2-perylene-quinone**, m.p. 187° is obtained by the oxidation of 1,12-dihydroxy-perylene (*Zincke*, Mo. 45, 231); **3,10-perylene-quinone** is obtained by oxidising perylene with chromic acid. Some 3,9-perylene-quinone is formed at the same time. The 3,10-compound is also obtained by treating 3,10-dibromoperylene with concentrated sulphuric acid at 130–140° (*Zincke*, Mo. 40, 408; Ber. 58, 328). **4,10-Perylene-quinone** is obtained from 4,10-dihalogeno-perylene (Ber. 58, 2389). **3,9-Perylene-quinone** and **3,4,9,10-perylene-diquinone** can be obtained from the corresponding halogen compounds (*Zincke*, Mo. 51, 77). Energetic oxidation of perylene with chromic acid gives 3,9-perylene-quinone and oxidises this further to anthraquinone-1,5-dicarboxylic acid, and partially through the 5,10-quinone to 1,9-benzanthrone-2-dicarboxylic acid-5,10. This last compound may be oxidised further to phenanthrene-1,8,9,10-tetracarboxylic acid (*Zincke*, Mo. 56, 143; 57, 405). For the hydrogenation of the perylene-quinones, see *Zincke*, Mo. 51, 280.

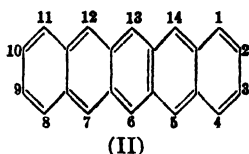
Of the carboxylic acids of perylene, **3,9-perylene-dicarboxylic acid**, m.p. 360°, is known (*Pongratz*, Mo. 48, 585). It was obtained from the 3,9-dibromoperylene through the dinitrile. For **perylene-mono- and -diphthaloyl-acids** and **3,9-diphthaloyl-perylene** obtained by heating with aluminium chloride, see *Zincke*, Mo. 48, 593. By the action of benzoyl chloride and aluminium chloride on pery-

lene, 3,9-dibenzoyl-perylene, m.p. 293°, together with a little 3,4-dibenzoyl-perylene, m.p. 330°, is formed. The latter gives 1,2-diphenyl-aceperylene,  $C_{24}H_{16}$  (I), m.p. 315–316°, in violet brown leaflets, when reduced by Clemmensen's method (Zincke, Mo. 56, 153; Ber. 58, 324).



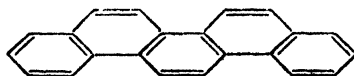
(*lin*-)2,3-6,7-Dibenzanthracene, or pentacene (II), is a deep-blue compound. The bi-radical nature of this substance which explains this property, can be confirmed by magnetic measurements (Müller, Ann. 517, 145).

With oxygen it forms a mono- and a bi-molecular peroxide. By condensation of pyromellitic anhydride with benzene and aluminium chloride, and subsequent ring-closure of the dibenzoyl-phenyl-dicarboxylic acid obtained, pentacene-5,7,12,14-diquinone, m.p. 408°, yellow needles, is formed. It passes into tetrahydro-pentacene, m.p. 244–245°, when reduced with hydriodic acid and phosphorus (Philippi, Mo. 32, 631; 34, 712; 35, 375; 42, 3). When distilled over



copper wool in a stream of carbon dioxide, 6,13-dihydropentacene, m.p. 270°, is obtained from it. By long keeping, 5,14-dihydropentacene, m.p. 310°, is formed. 6,13-Dihydropentacene is converted into pentacene on dehydrogenation with chloranil or benzoquinone. On oxidation with ferric chloride, 6,13-pentacene-quinone, m.p. 393°, is formed, whilst 5,14-dihydropentacene gives 5,7,12,14-pentacene-diquinone with chromic trioxide (Philippi, Mo. 53/54, 639; Clar, Ber. 63, 2967). For bromopentacene-diquinones and other derivatives of pentacene-quinone, see Philippi, Mo. 43, 615, 621; Seka, Mo. 47, 519, 627, 637.

Picene, 1,2-7,8-dibenzphenanthrene,  $C_{22}H_{14}$ , m.p. 364°, is obtained by distillation of lignite pitch and petroleum residues. It is made synthetically from naphthalene and ethylene bromide in the



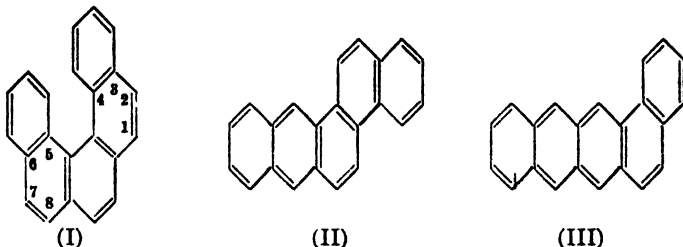
presence of aluminium chloride, by strongly heating 1,1'-naphthostilbene,  $C_{10}H_7 \cdot CH:CH \cdot C_{10}H_7$ , and by heating 1-methyl-naphthalene with sulphur (Lespieau, Bull. [3], 6, 238; Hirn, Ber. 32, 3341; Homer, J. 97, 1141).

Picene can also be obtained by the action of the Grignard compound of  $\beta$ -(naphthyl-1)-ethyl chloride and tetralone. With aluminium chloride in carbon disulphide, the reaction products gives picene (*Ruzicka*, *Helv.* 17, 470). It is difficultly soluble in the usual solvents, but dissolves best in crude cymol. It is reduced to **hydropicene**,  $C_{22}H_{24}$ , m.p.  $175^\circ$ , by hydriodic acid and phosphorus at  $250^\circ$ . Picene is oxidised to **picene-quinone** by chromic acid, and this compound, like the corresponding one of chrysene can be converted into picene ketone, **picene-fluorene-alcohol** and **picene fluorene**,  $(C_{18}H_{14})_2CH_2$ , on the one hand, and **picenic acid**, or **dinaphthyl-carboxylic acid** and **2,2'-dinaphthyl** on the other (*Chattaway*, *Ber.* 26, 1751):



**3,4,5,6-Dibenzphenanthrene (I)**, m.p.  $177-178^\circ$ , is obtained from di-*o*-aminobenzylidene-*p*-phenylene-diacetic acid by diazotisation and decomposition of the resulting compound with copper powder. The di-carboxylic acid thus formed is distilled, when it gives (I) and **1,2,5,6-dibenzanthracene** (see below) (*Hansging*, *Mo.* 39, 323). **3,4,5,6-Dibenzphenanthrene-diquinone-1,2,7,8**, m.p.  $360^\circ$  dark red needles, see *Cook*, *J.* 1933, 1592.

**1,2,6,7-Dibenzphenanthrene**, greenish-yellow leaflets, m.p.  $293-294^\circ$  (II), and **1,2,6,7-dibenzanthracene**, yellow leaflets, m.p.  $263-264^\circ$  (III) are produced together with **1,2,3,4-dibenzanthracene** (see below) by the internal condensation of *o*-toluyl-phenanthrene with elimination of water. Compound (III) can also be obtained from 2-methyl-3- $\alpha$ -naphthoyl-5,6,7,8-tetrahydronaphthalene or the corresponding  $\beta$ -compound by heating with copper powder (*Naturkupper C*) (*Clar*, *Ber.* 62, 354, 1574; 65, 1411). **1,2,6,7-Dibenzanthracene** and **1,2,5,6-**



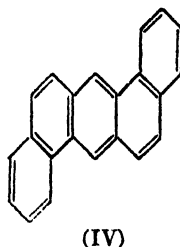
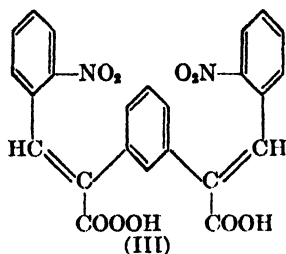
**dibenzanthracene**, and possibly the **1,2,7,8-compound** are obtained by condensation of 1-chloromethyl-naphthalene with 2-methyl-naphthalene in carbon disulphide with aluminium chloride. A mixture of two isomeric dinaphthylmethanes is formed, which on dehydrogenation with copper powder gives the above hydrocarbons. They can be separated by their different reactivities towards maleic anhydride (*Clar*, *Gazz.* 62, 539).

**1,2,7,8-Dibenzanthracene**,  $C_{22}H_{14}$ , m.p.  $196^\circ$  (I) is obtained from 1,1'-dinaphthyl-ketone-2-carboxylic acid (II) by reduction of the CO group to  $CH_2$ , ring-closure to the anthrone, and subsequent distillation with zinc dust. Another



method starts with the condensation of *m*-phenylene-diacetic acid and *o*-nitrobenzaldehyde. The nitro-groups in the condensation product (III) are reduced to amino-groups, and the amine submitted to the *Pechorr* phenanthrene synthesis.

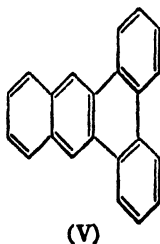




In this way small quantities of 1,2-7,8-dibenzanthracene-4,5-dicarboxylic acid are obtained, which on heating loses carbon dioxide and gives the required substance. 1,2-7,8-Dibenzanthraquinone, m.p. 225–226°, forms orange needles (Cook, J. 1932, 1472).

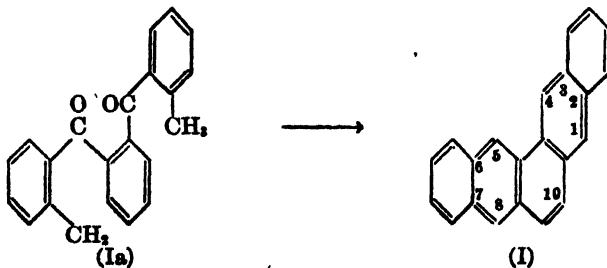
1,2-5,6-Dibenzanthracene (IV), m.p. 262°, picrate, m.p. 214°, is obtained by heating 2-methyl-1,2'-dinaphthyl-ketone, m.p. 170–171°. The naphthyl-ketone itself is obtained by the action of  $\beta$ -naphthoyl-chloride on  $\beta$ -methyl-naphthalene in the presence of aluminium chloride (Clar, Ber. 62, 350; Fieser, Ber. 62, 1827; Cook, J. 1931, 487; Clar, Gazz. 62, 539). By the action of nitric acid on the hydrocarbon, 9-nitro-1,2-5,6-dibenzanthracene, m.p. 217–218°, is formed. For other derivatives, see Cook, J. 1931, 489, 3273. They show a characteristic fluorescence spectrum, and are carcinogenic compounds. Reduction of 1,2-5,6-dibenzanthracene with sodium and amyl alcohol gives rise to an octa-hydro-derivative.

By condensation of naphthalene-1,2-dicarboxylic anhydride and naphthalene, a ketonic acid is obtained, which, on ring-closure gives a mixture of 1,2-7,8- and 1,2-5,6-dibenzanthraquinone, m.p. 224–225°, reddish needles (Lauer, J. pr. [2], 135, 1). 1,2-3,4-Dibenzanthracene (V), m.p. 205°, colourless needles, picrate, m.p. 207°, is obtained by the action of *o*-toluyl-chloride on phenanthrene in the presence of aluminium chloride. On heating the mixture of ketones produced, a



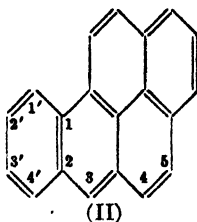
mixture of hydrocarbons is obtained, of which the chief constituent is 1,2-3,4-dibenzanthracene. The separation of the isomeric hydrocarbons is best carried out with maleic anhydride. The 1,2-3,4-compound reacts the most rapidly, while 1,2-6,7-dibenzanthracene reacts much more slowly (Clar, Ber. 62, 350; 65, 1411). For quinones of 1,2-3,4-dibenzanthracene see Clar, *loc. cit.*

2,3-6,7-Dibenzphenanthrene (I), m.p. 257°, yellowish-green needles or leaflets,

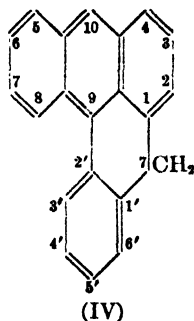
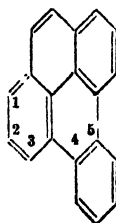


picrate, m.p.  $184^{\circ}$ , can be obtained by heating di-*o*-toluyl-benzenes (Ia), which are obtained by acting on *sym*-phthalic anhydride, terephthalic anhydride or isophthalic anhydride with *o*-tolyl magnesium bromide (*Clar*, Ber. 62, 940, 3021; 64, 981). For derivatives of this hydrocarbon, see *Clar*, loc. cit.

1,2-Benzpyrene (II), m.p.  $176^{\circ}$ , picrate, m.p.  $230^{\circ}$ , is found in coal-tar and has powerful carcinogenic properties.



It has been obtained synthetically by condensation of pyrene with succinic anhydride, giving  $\beta$ -(1-pyrenoyl)-propionic acid. The sodium salt of this is reduced by zinc dust and ammonia to the hydroxy-acid. By removal of water from this, followed by hydrogenation,  $\gamma$ -(1-pyrenyl)-butyric acid is formed. When this is treated with stannic chloride at  $120^{\circ}$ , 4-keto-1',2',3',4'-tetrahydro-1,2-benzpyrene is formed, and this, when dehydrogenated with selenium gives 1,2-benzpyrene (*Cook*, J. 1933, 395):



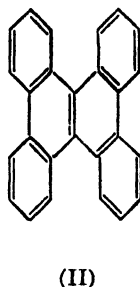
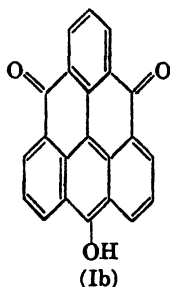
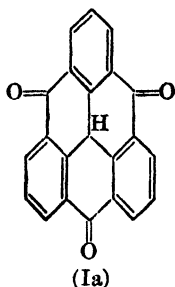
4,5-Benzpyrene (III), m.p.  $178-179^{\circ}$ , picrate, m.p.  $228-230^{\circ}$ , is also found in coal-tar. The synthesis starts from *sym*-hexahydropyrene, which condenses with succinic anhydride to give  $\beta$ -1,2,3,6,7,8-hexahydro-4-pyrenoyl-propionic acid. The latter is reduced by the Wolff-Kischner method, and the ring closed with sulphuric acid. The 1'-keto-1,2,3,6,7,8,1',2',3',4'-decahydro-4,5-benzpyrene is reduced with sodium and alcohol, and dehydrogenated with selenium, when 4,5-benzpyrene results (*Cook*, J. 1933, 395).

Coeranthrene (IV) (*peri*-benzylene-anthracene) itself is not known, but derivatives of it have been obtained. Thus, 2-methyl-coeranthrene-7',  $C_{22}H_{14}O$ , m.p.  $175-176^{\circ}$ , bright red to yellowish-brown leaflets with a coppery lustre, is obtained by the action of concentrated sulphuric acid on 2-methyl-9-phenylanthracene-1-carboxylic acid, m.p.  $282^{\circ}$ . For other derivatives, see *Scholl*, Ann. 493, 56.

### (c) Systems with Six or More Rings

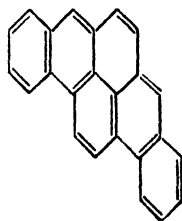
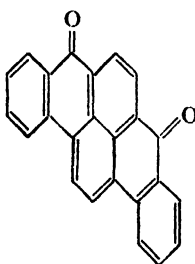
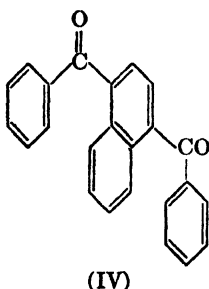
Trimethylene-triphenylmethane-triketone (I) is a derivative of this class, and is to be regarded as derived from triphenylmethane, in which the phenyl nuclei are linked up with CO groups. It forms dark blue needles, melting above  $450^{\circ}$ . It is obtained by the action of concentrated sulphuric acid on triphenylmethane-

2,2',2''-tricarboxylic acid (*Weiss*, Mo. 45, 207; 47, 307), and occurs also in the isomeric hydroxy-diketo-form (*Weiss*, Mo. 65, 129) (Ib):

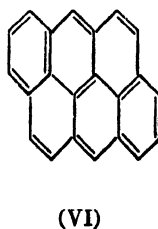
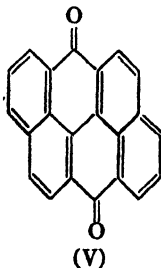


**Biphenylene-phenanthrene (II)**, picrate, m.p. 200°, is obtained as a by-product in the preparation of rubicene (p. 691) from fluorene, or from the same starting materials, together with dibiphenylene-ethane (p. 680) by heating with copper bronze (*Bergmann*, Ann. 483, 72).

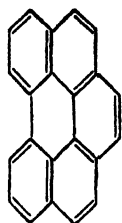
**4,5-8,9-Dibenzpyrene (III)**, m.p. 282°, is obtained from the 3,10-quinone by distillation in steam over zinc-pumice stone. This quinone is obtained by heating 1,4-dibenzoyl-naphthalene (IV) with aluminium chloride (*Scholl*, Ber. 55, 118).



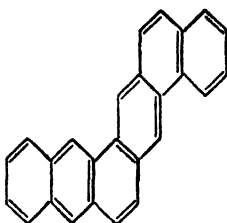
**Anthanthrone (V)**, m.p. above 300°, forms orange coloured spikes, and is a good vat-dye like pyranthrone (p. 710). It is obtained from 1,1'-dinaphthyl-2,2'- or -8,8'-dicarboxylic acid with acid condensing agents (*Kalb*, Ber. 47, 1724). On treatment with hydriodic acid and phosphorus and subsequent dehydrogenation with copper, the parent hydrocarbon, **anthanthrene (VI)**, m.p. 257°, is obtained in golden-yellow leaflets (*Scholl*, Ber. 67, 1232).



**1,12-Benzperylene (VII)**, m.p. 273°, yellowish-green plates with a blue fluorescence, picrate, m.p. 267°, is obtained from the maleic anhydride addition product of perylene (p. 701) by heating it with soda-lime (*Clar*, Ber. 65, 846).



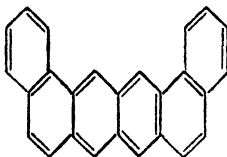
(VII)



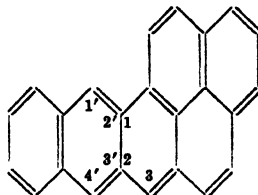
(VIII)

1,2-(Phenanthro-2,3)-anthracene (VIII),  $C_{26}H_{18}$ , m.p.  $281-282^\circ$ , yellow needles, is obtained by heating the reaction product of 1-anthroyl-chloride and 2-methyl-naphthyl-(1)-magnesium bromide to  $430^\circ$  to  $450^\circ$  (Cook, J. 1931, 499).

2,3-(Phenanthro-2,3)-phenanthrene (IX),  $C_{26}H_{18}$ , m.p.  $341-343^\circ$ , yellow needles, is obtained from 3-(2-methylnaphthoyl-1)-phenanthrene by heating to  $450^\circ$ . The latter compound is obtained from 3-phenanthroyl chloride and 2-methylnaphthyl-(1)-magnesium bromide (Cook, J. 1931, 499).



(IX)

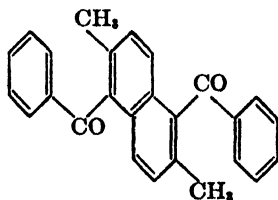


(X)

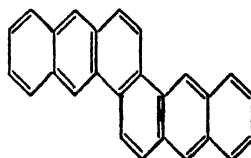
(2',3'-Naphtho-)-1,2-pyrene (X), m.p.  $273^\circ$ , deep orange needles, is obtained by condensation of pyrene and phthalic anhydride. The phthaloyl acid thus obtained is reduced and cyclised to the anthrone, and the latter is then reduced to (2',3'-naphtho-)-1,2-pyrene. It is also produced by the pyrolysis of the mixture of ketones obtained from *o*-toluyl chloride and pyrene. In contrast to 1,2-benzpyrene, the hydrocarbon has no carcinogenic properties, and gives an addition compound with maleic anhydride (Cook, J. 1933, 395).

In the same way as five-condensed-ring systems can be obtained from di-*o*-toluyl-benzenes by double ring-closure (Clar, Ber. 62, 940), the ring-closure of dibenzoyl-dimethyl-naphthalenes on heating and loss of two molecules of water, gives rise to hydrocarbons with six condensed nuclei.

Thus, anthraceno-1,2-1',2'-anthracene (I), yellow leaflets, m.p.  $400^\circ$ , is obtained from 1,5-dibenzoyl-2,6-dimethylnaphthalene, m.p.  $263-264^\circ$  (Ia), and from 1,8-dibenzoyl-2,7-dimethyl-naphthalene

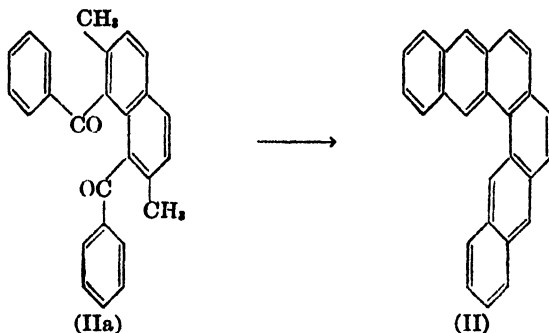


(Ia)

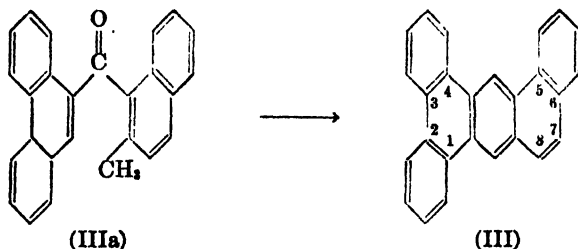


(I)

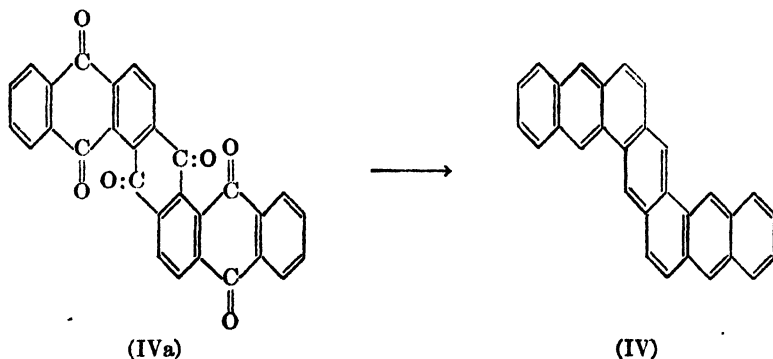
(IIa), an isomeric anthraceno-1,2-1',2'-anthracene (II), m.p. 308° is formed (Clar, Ber. 62, 950; Fieser, Ber. 62, 1828).



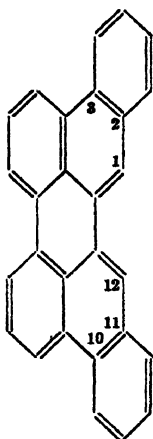
In the same way 1,2-3,4-5,6-tribenzanthracene (III), m.p. 224°, is obtained from 2-methyl-1-(phenanthroyl-9')-naphthalene. The ultra-violet absorption curves have proved very useful for the characterisation of these complicated ring systems.



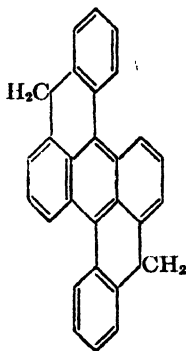
Dinaphtho-2',3'-1,2-2',3'-5,6-anthracene (IV),  $C_{30}H_{18}$ , orange needles, is obtained from 1,2-5,6-diphthaloyl-anthraquinone (IVa) with hydriodic acid and



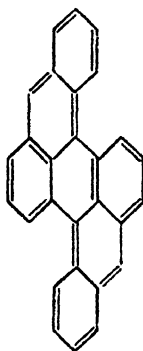
anthracene-dicarboxylic acid. Dibromo-hetero-coerdianthrone is another derivative, which forms bluish-violet crystals. Hetero-7,7'-dianthrone gives 1,2-7,8-dibenzperylene (VII) in dark yellow needles, when treated with hydriodic acid and phosphorus and subsequent distillation with zinc dust.



(V)

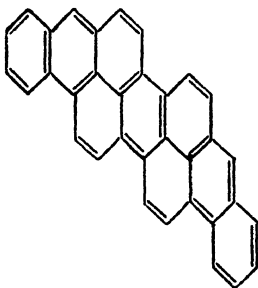


(VI)

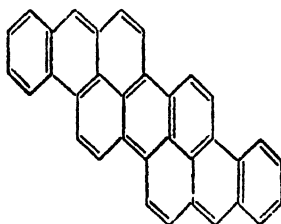


(VII)

The hydrocarbon of violanthrone (p. 698) is violanthrene (VIII), which has been obtained in red leaflets. It is prepared by reduction of violanthrone with hydriodic acid and phosphorus and subsequent dehydrogenation with copper.



(VIII)



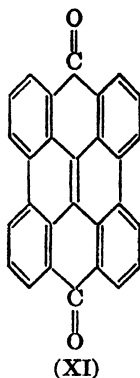
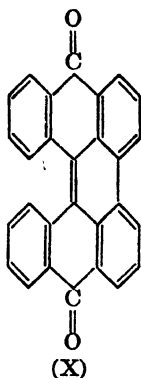
(IX)

The hydrocarbon of isoviolanthrone (p. 698) is isoviolanthrene (IX), bluish-red leaflets. It is obtained from isoviolanthrone by reduction with hydriodic acid and phosphorus and subsequent dehydrogenation with copper (*Scholl, Ber. 67, 1232*).

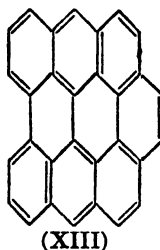
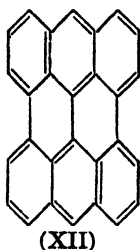
A group of important compounds with seven and eight condensed rings are obtained from the dianthraquinoyls. They are used as vat dyes. These compounds are characterised by the fact that they readily pass into quinone-like compounds of highly condensed systems by repeated fusion of the anthraquinone nuclei.

Thus, 1,2'-dianthraquinoyl gives on reduction with copper or nickel powder and concentrated sulphuric acid, meso-benzdianthrone or helianthrone (X). This compound forms steel-blue crystals which form haematite-like masses from xylene, and resembles meso-dianthrone in structure. It can also be obtained by the reduction of 1,1'-dianthraquinoyl with sodium hydrosulphite in a current of coal-gas, and dropping dilute sulphuric acid into the hot solution (*Eckert, J. pr. [2]*).

121, 273). For hydroxy-helianthrones, see *Hardacre*, J. 1929, 180; *Haller*, J. 125, 231.



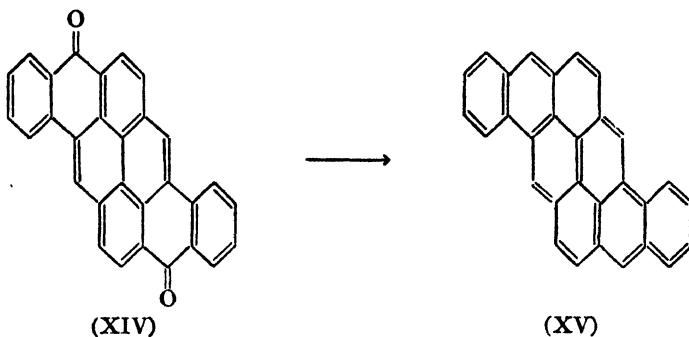
When heated with aluminium chloride to 140–145°, helianthrone splits off two hydrogen atoms, and with repeated combination of two benzene nuclei, **meso-naphthodianthrone** (XI) is formed in brown needles (*Scholl*, Ber. 43, 1734). It can be obtained more simply by irradiating helianthrone with ultra-violet (*Meyer*, Mo. 33, 1447), and by distillation of 1,1'-dianthraquinoyl with zinc dust (*Scholl*, Ber. 52, 1829). For chloro-derivatives of meso-naphthodianthrone, see *Eckert*, Mo. 39, 839. The parent hydrocarbon of meso-naphthodianthrone is **meso-naphthodianthrene** (XII), which forms dark blue crystals with a violet lustre. It is obtained from the ketone by reduction with hydriodic acid and phosphorus, when **hexahydro-meso-naphthodianthrene** is obtained in golden yellow leaflets, which on dehydrogenation with copper forms meso-naphthodianthrene (*Scholl*, Ber. 67, 1236).



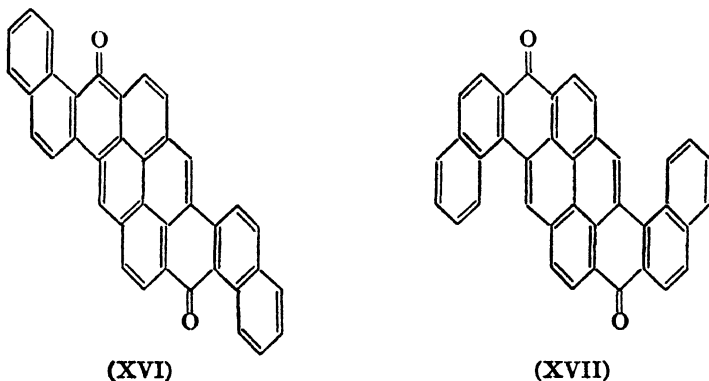
Meso-naphthodianthrene gives an addition product with maleic anhydride, which, when distilled with soda-lime gives **meso-anthrodianthrene** (XIII) (2,3,4,5[*vic-di-peri*]-dibenzcoronene), in bluish-violet needles. It can also be prepared from meso-anthrodianthrene by the action of hydriodic acid and phosphorus and dehydrogenation with copper (*Scholl*, Ber. 67, 1232, 1236).

2,2'-Dimethyl-1,2'-dianthraquinoyl condenses on heating alone, or better when boiled with concentrated alcoholic potash, splitting off 2H<sub>2</sub>O, and becoming pyranthrone (XIV), reddish-brown needles, which is similar in structure to flavanthrene (p. 658) and bears the same relationship to this substance as anthraflavone does to indanthrene (p. 658) (*Scholl*, Ber. 43, 346). It can also be obtained by heating 3,8-dibenzoylpyrene with aluminium chloride to 155–160° (*Scholl*, Ann. 394, 121). The parent hydrocarbon of pyranthrone is **pyranthrone** (XV), reddish-brown needles. It is obtained from

pyranthrone by reduction with hydriodic acid and phosphorus and subsequent dehydrogenation with copper (*Scholl*, Ber. 67, 1232).

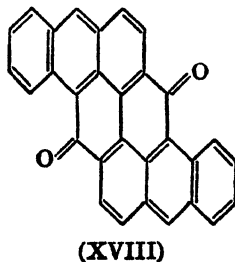


If 3,8-di- $\alpha$ -naphthoyl- and 3,8-di- $\beta$ -naphthoyl-pyrene are treated with aluminium chloride at 160°, the still more highly condensed systems of 5,6-5',6'-dibenzpyranthrone (XVI) and 7,8-7',8'-dibenzpyranthrone (XVII) are formed.



All these compounds are vat dyes, and pyranthrone particularly is used industrially under the name indanthrene golden-orange. It is a very fast dye.

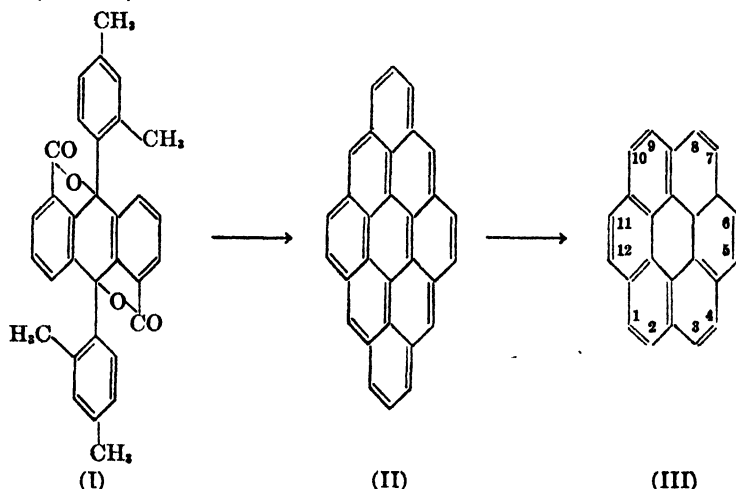
*amphi-Isopyranthrone* (XVIII) is an isomeric pyranthrone, which is obtained by heating 1,1'-bianthryl-2,3'-carboxylic acid with phosphorus pentoxide or aluminium chloride. It forms greyish-violet tablets with a metallic lustre, and dissolves giving a fuchsine red solution. It has none of the properties of quinones. For reduction products of *amphi-iso*-pyranthrone, and for *dihydro-iso*-pyranthrone, see Ann. 433, 163. The latter is obtained by reducing *amphi-iso*-pyranthrone with hydriodic acid.



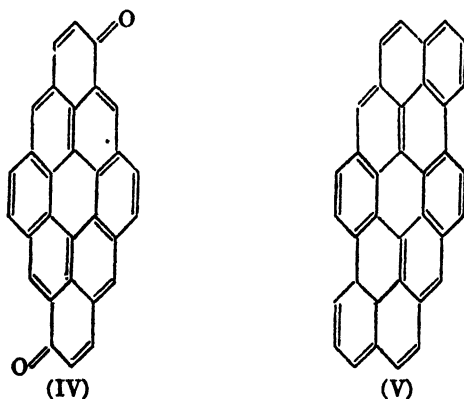


A very interesting compound is the hexabenzobenzene, **coronene** (III),  $C_{24}H_{12}$ , so named because the outer ring of benzene nuclei forms a crown. It crystallises in yellow needles, m.p. 416–417°, and dissolves in organic solvents with a bluish-violet fluorescence. Its considerable stability is expressed in its formula, being built up of two concentric rings of carbon atoms, an inner one with the configuration of benzene, and an outer one with 18 carbon atoms, with the same arrangement of bonds as in benzene.

The compound can be synthesised from 9,10-di-*m*-xyl-9,10-dihydroxy-9,10-dihydro-anthracene-1,5-dicarboxylic lactone (I), which is readily obtained from anthraquinone-1,5-dicarboxylic chloride, *m*-xylene, and aluminium chloride. Through a series of intermediate stages, 2,3,8,9-dibenzcoronene (II) is obtained. This is converted into the 2,3,8,9-dibenzcoronene-quinone, which on oxidation gives the 2,3,8,9-tetracarboxylic acid, from which coronene (III) is obtained (Scholl, Ber. 65, 902).



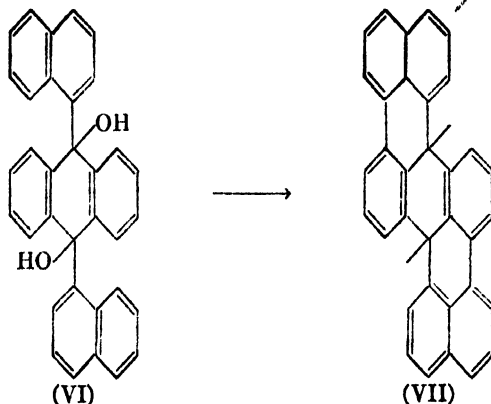
In contrast to coronene, **dibenzcoronene** is a very reactive substance. It forms red needles with an emerald green lustre, and its solution is sensitive to light. Oxygen readily converts it into **dibenzcoronene-quinone** (IV). For O- and S-isologues of dibenzcoronene, see Scholl, Ber. 67, 599.



The hydrocarbon the most rich in carbon is 1,2,3-7,8,9-dinaphthocoronene (V), which crystallises in chestnut brown needles. It is obtained from 1,2,3-7,8,9-

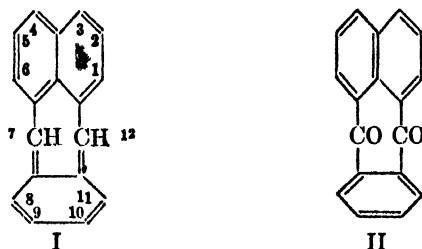
dinaphtho-coronene-quinone-(4,10) by reduction with hydriodic acid and phosphorus and dehydrogenation with copper. The quinone is formed, together with other substances, by the action of 1,5-anthraquinone-dicarboxyl chloride, on naphthalene in the presence of aluminium chloride, the reaction being carried out in nitrobenzene solution (*Scholl*, Ber. 67, 1232).

1,9-5,10-Di-(perinaphthylene)-anthracene (VII), m.p. in a sealed tube 580° after sintering at 300°, forms leaflets with a coppery lustre, dissolving to give a deep greenish-blue solution. It is obtained from 9,10-di- $\alpha$ -naphthyl-9,10-dihydroxy-9,10-dihydroanthracene (VI) by heating with aluminium chloride and some pyridine.



The substance has been formulated as a bi-radical (VII). It reacts rapidly with maleic anhydride. Absorption spectra, however, show that the radical character of the substance is not very definite, and moreover, it does not react with oxygen. The compound has been referred to as "the link between the aromatic compounds and graphite" (*Clar*, Ber. 65, 1521).

Pleidene (I) is made up of three benzene nuclei and a seven-membered ring. Only derivatives of this compound are known. Pleiadene is obtained from 2- $\alpha$ -naphthoyl-benzoic acid by reduction of the CO group to CH<sub>2</sub>, and cyclising. It



very readily passes into pleiadene-dione (II) on oxidation. 1-Methyl-pleiadene-7, m.p. 128°; 1,2-dimethyl-pleiadene, m.p. 192°; 1-methyl-pleiadene-dione-7,12, m.p. 183° (*Riche*, Ber. 65, 1371; *Fieser*, Am. 55, 3010).

For further highly condensed systems, with six, seven, and poly-membered rings, see *Fieser*, Ber. 62, 1827; *Clar*, Ber. 63, 112. For the quinones of these compounds see the above references, and *de Diesbach*, Helv. 7, 644; 11, 724; *Scholl*, Ber. 61, 2550.



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